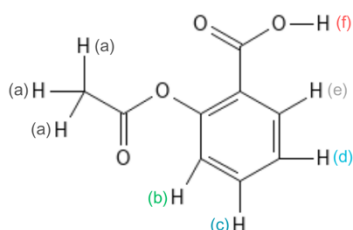


Name: Harsh Agrawal

CID: 02320622

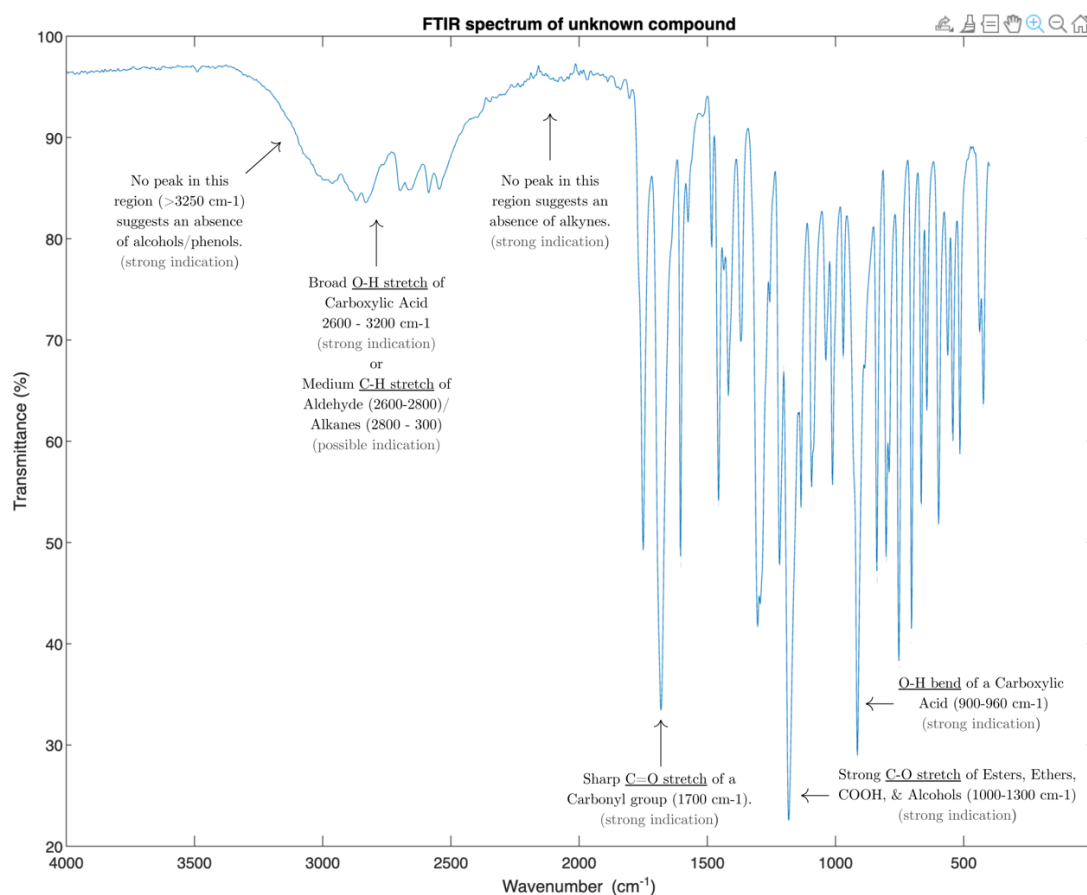
Proposed structure (with different proton environments labelled as H_A , H_B , H_C etc.). Chemical formula is $C_9H_8O_4$



IUPAC Name: 2-acetoxybenzoic acid

Common Name: Aspirin

Annotated FTIR spectrum



Analysis:

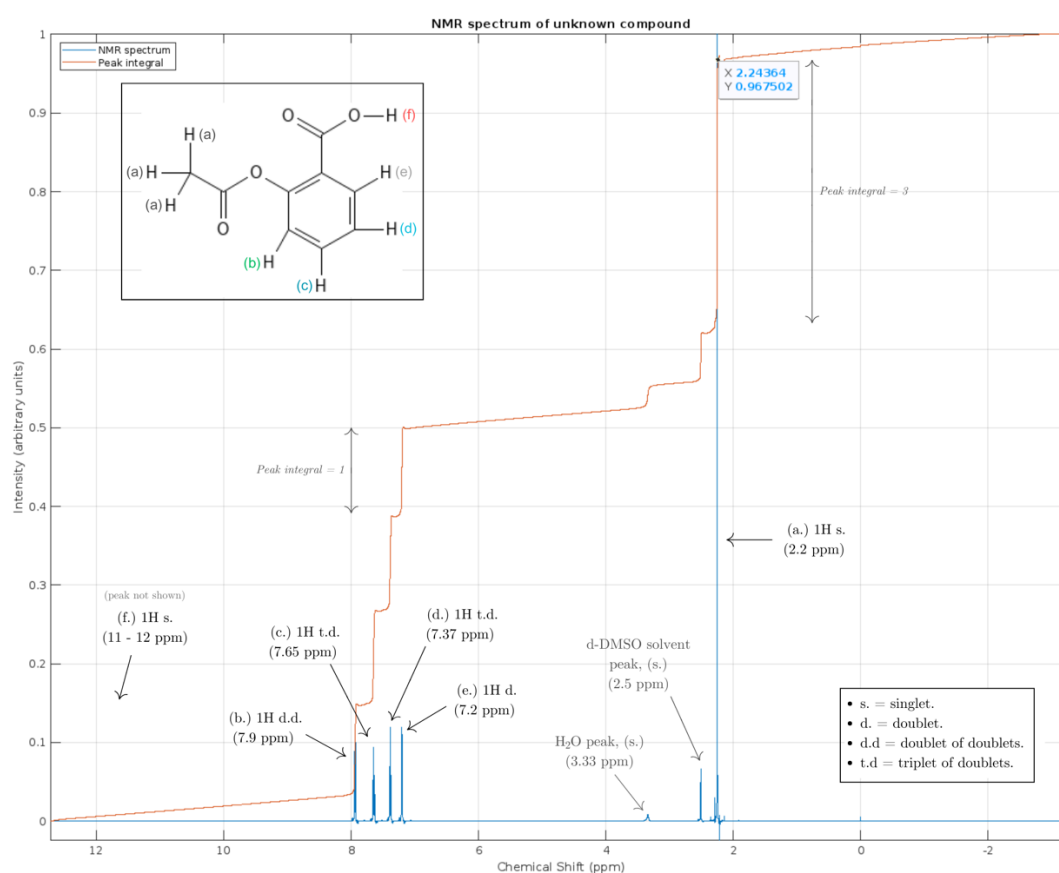
A broad peak near the $2600-3200\text{ cm}^{-1}$ strongly demonstrates the O-H stretch of the carboxylic acid as there is no nitrogen present and there are no other prominent functional groups in that region. The absence of any deterministic peak in the region $>3250\text{ cm}^{-1}$ indicates the absence of the alcohols and phenols.

The sharp peak at 1700 cm^{-1} strongly matches with the presence of the C=O stretch for a Carbonyl group (of ketones, aldehydes). Similarly the sharp peak in the fingerprint region at $\sim 1200\text{ cm}^{-1}$ suggests the C-O stretch of Carboxylic Acid, or of ethers, esters, and alcohols. This coupled with the first observation and another peak for O-H bend for COOH ($\sim 940\text{ cm}^{-1}$) confirms the presence of carboxylic acid in the molecule.

The other peaks also strongly suggest the presence of another Carbonyl group, but the exact functional group can't be strongly determined with Ketones, Aldehydes being plausible contenders. The spectrum doesn't show any indications for Alkynes. There is a short albeit sharp peak near 1450 cm^{-1} that might indicate the presence of an aromatic ring.

The reference table was obtained from (Mohrig 2009)

NMR peak table



Assigned proton(s)	Chemical shift (ppm)	Multiplicity	Coupling constant(s) (Hz)	Integral (H)
H _A	2.20	Singlet	-	3
H _B	7.90	Doublet of Doublets	7.8 (big), 1.8 (small)	1
H _C	7.65	Triplet of Doublets	7.2 (big), 0.6 (small)	1
H _D	7.37	Triplet of Doublets	7.2 (big), 1.2 (small)	1
H _E	7.20	Doublet	6	1

Two additional Peaks (not belonging to the molecule): 1-H Singlet at 3.33 PPM, 1-H singlet at 2.5ppm

Analysis:

From the H-NMR spectrum, four 1-H peaks (with variable multiplicity) and one 3-H peak (singlet) were identified. Additionally, two extra peaks were observed (not attributable to the molecule as their peak integrals were < 1). One 1-H peak was absent, leaving the total at 7H instead of the required 8H. An initial estimation suggested an aromatic compound based on identifying four peaks (labelled b, c, d, e) within the chemical shift range of 7-8ppm. Since four distinct 1-H peaks were present, it was inferred that two different functional groups might be attached to the aromatic (benzene) ring, likely in either ortho or meta positions, ensuring four unique hydrogen environments. The para position was ruled out, as it would yield symmetrical aromatic compounds, resulting in 2 x 2H peaks instead of 4 x 1-H peaks.

Peak a (3-H singlet), located at a chemical shift of 2.2ppm, strongly suggested a relatively de-shielded methyl group. To maintain singlet multiplicity, the methyl group must be four bonds away from a hydrogen and likely bound to an electronegative atom causing its de-shielding from the original position of ~ 1.5 ppm.

FTIR indicated a significant presence of carboxylic acid. This finding supported the hypothesis that the missing H-peak could belong to the hydrogen of the COOH group, expected around 11-12ppm. If COOH is directly attached to the benzene ring, then the hydrogen of the carboxylic acid would be five bonds away from the nearest hydrogen of the aromatic ring, suggesting a singlet multiplicity for the missing H peak.

The primary challenge involved resolving the two doublet and two triplet 1-H peaks. Assuming only hydrogens in identical environments can split the peak made this configuration impossible, as all four hydrogens in this molecule belonged to different chemical environments. It was then assumed that hydrogens in similar (though not identical) environments could also split a peak. Considering this, the only feasible outcome was if the hydrogens with triplet peaks were sandwiched between those with doublet peaks, allowing the triplet hydrogens to split themselves and the neighbouring hydrogen (with the doublet peak). The doublet peaks of the outward hydrogens could be explained if they were adjacent to a carbon without a hydrogen. For one of the doublet hydrogens, this was explainable by a carboxylic acid attached to the adjacent carbon. This suggests that the other functional group is located at the ortho position next to the carbon with COOH. If it were at the meta position, one of the doublet 1-H peaks would be converted to a singlet, and a triplet to a doublet, respectively.

To complete the molecule, given that COOH is a terminal functional group, the remaining functional group must contain two oxygen atoms, one carbon atom, and a methyl group. To prevent splitting of hydrogens in the methyl group, it should likely be terminal (ensuring > 4 bonds away from the hydrogen from benzene). This left the possibility for either an oxygen or a carbon to be connected to the benzene ring with a carbonyl group on the carbon. In the former structure the methyl group is attached to the Carbon whereas in the latter it's attached to an Oxygen. Unable to deterministically resolve this choice through NMR or FTIR, melting point and R_f values were searched on PubChem for both variants, and the variant with oxygen connected to the benzene group was finally chosen because of close match. This helped resolve the mystery molecule – Aspirin!

This molecular configuration also explains the second-order splitting (triplet of doublets) for the sandwiched hydrogens, as they are first split into triplets (as explained above) and then further split into a doublet by the second neighbouring hydrogen. The unexplained bit still remains to understand

why one of the doublet peaks is a doublet of doublets while the other one is definitely a pure doublet. Ideally, they should've both been either pure doublets or doublet of doublets.

The missing peak at 11-12 ppm would also account for the uneven peak integrals. Without the peak, the peak integrals were ~1.15 rather than close to 1. If another peak is added and the peak integral curve is normalized, the value should be much closer to 1.

The remaining two peaks (not belonging to the molecule) were identified by consulting a reference contaminant table (Goldberg 2010). The first peak (at 2.5 ppm) belongs to the solvent (d-DMSO), while the second small peak (at 3.33 ppm) belongs to water. Both are explained in the questions segment.

The reference table was obtained from (Mohrig 2009)

Other data

Property	Value
R _f	0.54
Melting point (°C)	120

Analysis:

Both Thin Layer Chromatography and Melting Point assessment elaborate on the purity of the compound. The melting point of the compound ranged between 115 – 128 °C which clearly indicates that the sample isn't pure as the melting point range for a pure sample should be within 1-2 °C. The melting point of Aspirin is referenced as 136 °C which is > 15 °C higher than the pure compound denoting the poor purity of the compound. (Catherine 2021). Similarly, the R_f value we obtained was 0.54 as compared to 0.44 referenced for pure Aspirin (Lipsy 2005). Typically an R_f value of 0.54 denotes a moderately polar compound, as it is retained to a moderate extent by the stationary phase (the TLC plate) compared to the mobile phase (the solvent). However, this fact, isn't very useful in determining the structure of the molecule of interest.

Questions

1. What would the main differences be in the NMR spectrum if we used a 60MHz spectrometer as opposed to a 600MHz spectrometer?

For a 600MHz spectrometer, 1 ppm correlates to 600Hz, which is sufficiently high to resolve peaks and their multiplicity properly. The primary difference, if a 60MHz spectrometer is used, would be the resolution of the spectrum. With a 10x lower field strength, the signals would be substantially broader, and the peak multiplicity might not be resolved properly. Peaks closer together might be obtained as one single spread-out peak (triplets would look like singlets). This is also due to the coupling constants being 10x lower, thus hindering signal resolution. The signal-to-noise ratio would also decrease (ResearchGate 2020).

2. There are at least two peaks in the NMR spectrum which do not belong to the molecule. Where might they have come from?

The first peak (2.5ppm) is the solvent (d-DMSO) peak itself. The peak arises as the commercially available d-DMSO isn't 100% deuterated and thus the un-deuterated Hydrogens show up as a singlet peak near 2.5 ppm (Goldberg 2010).

The second peak almost certainly belongs to water (3.33 ppm) that results in interaction between water and solvent molecules. Since it's tightly bound to DMSO by hydrogen bonding, the chemical shift isn't affected as much as in polar solvents such as CDCl₃. (Goldberg 2010)

3. Why does the location of the mystery compound show up as a dark spot under UV illumination of the plate?

The TLC plate is coated with a fluorescence material (most probably zinc sulphide) which fluoresces by absorbing UV light (wavelength ~250nm) and re-emitting at a longer wavelength. When the compound travels up the UV plate, and is irradiated with UV light, it absorbs the UV light preventing the fluorescent material in turn to absorb the UV light. This is why the patch where the compound is present appears as a dark spot under UV whereas the rest of the plate fluoresces. Thus, even the line through which the compound travels up also look visibly dark under UV.

4. Why is the melting point of a contaminated sample very rarely higher than the pure compound?

A pure compound forms a highly ordered and stable crystal lattice. This requires a high energy to break down these bonds to liquify the material. When introduced to contaminants, this lattice becomes less ordered as the contaminants occupy within the lattice. This is why, after the contaminant introduction, the force, and thus energy, required to break these bonds almost always goes down. Thus, the melting point of a contaminated sample very rarely higher than the pure compound.

Works Cited

- Goldberg, Karen I. 2010. "NMR Chemical Shifts of Trace Impurities: Common Laboratory Solvents, Organics, and Gases in Deuterated Solvents Relevant to the Organometallic Chemist." *Organometallics* 2176–2179.
- ResearchGate. 2020. *Comparison of 60 MHz (benchtop) and 600 MHz (high-field) 1 H NMR spectra*. https://www.researchgate.net/figure/Comparison-of-60-MHz-benchtop-and-600-MHz-high-field-1-H-NMR-spectra-obtained-from-an_fig6_365436418.
- Catherine, Saangi. 2021. "Physical and Chemical Properties of Aspirin." *Journal of Clinical and Experimental Pharmacology* 164.
- Lipsy, Peter. 2005. *Thin Layer Chromatography Characterization of the Active Ingredients in Excedrin and Anacin*. Department of Chemistry and Chemical Biology, Stevens Institute of Technology, Castle Point on Hudson, Hoboken, NJ 07030, USA.
- Mohrig, Jerry R. 2009. *Figures from Techniques in Organic Chemistry, third edition*. <https://cpb-us-e1.wpmucdn.com/sites.ucsc.edu/dist/9/291/files/2015/11/IR-Table-1.pdf>.