Research Paper | Chemistry

Axial & Equatorial Protons Coupling Studies of 1-(2-Fluoro-4-Nitrophenyl)-N,N-Dimethylazetidin-3-Amine Using Decoupling Technique of Nmr Spectroscopy

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ABSTRACT *The chemical-shift difference, δae between the axial and the equatorial protons has been always a matter of discussion . In virtually every case, the shielding contribution to δae (β)from the C-X bond appears to have the opposite sign from that to δae(α). There are reasonable grounds to exclude an electric field effect or a directed inductive effect as the cause of this sign reversal. A model for diamagnetic anisotropy with the principal axis of magnetic susceptibility along the C-X bond can also be excluded, since it predicts identical effects on δae(α) and δae (β)*

KEYWORDS: Chemical shift; axial; equatorial; shielding; anisotropy

Introduction:

A simplified [1] yet convenient description of how spin decoupling operates considers two spin-½ nuclei, A and X, that share a mutual scalar coupling of J Hz. The resonant frequency of the X spins will depend on whether their coupled partners are oriented parallel (α orientation) or anti-parallel (β orientation) to the applied static field. For a spin ensemble we can assume there exists an equal number of A nuclei in the α and β states, owing to the very small energy difference between the two orientations, and thus the X spectrum displays the familiar doublet pattern. Application of an rf field, designated the B_2 field (recall the transmitter field is termed B_1), at the frequency of the A spins causes these to undergo continuous, rapid transitions between the α and β orientations by continually inverting these spins. If this reorientation is fast relative to the coupling constant, the X spin doublet coalesces into a singlet since the lifetimes of the α and β orientations are no longer sufficient for the coupling to be distinguished. Thus, if the A spins are irradiated during data acquisition with a sufficiently strong field such that $\gamma B_2 > J$ Hz, the X resonance displays no coupling to A and the spins are said to be decoupled.

Whilst the removal of scalar spin–spin coupling is the usual goal of such experiments, a number of additional effects can arise from the application of the additional rf field, which may be beneficial or detrimental depending on the circumstances. Incomplete decoupling can introduce residual line broadening or, even worse, leave rather esoteric partially decoupled multiplets, whilst the non-uniform irradiation of a resonance can introduce population transfer effects that cause intensity distortions within multiplets . Population disturbances caused by the rf may also produce intensity changes that arise from the NOE,which operates quite independently from J-coupling. Finally, changes in the resonant positions of signals close in frequency to the applied rf may also be observed, so-called Bloch–Siegert shifts.

Homonuclear decoupling involves the selective application of a coherent decoupling field to a target resonance with the aim of identifying scalar spin-coupled partners, and is most often applied in proton spectroscopy. Although the use of this method for identifying coupled 1H–1H spins has been largely superseded by 2D correlation methods, selective decoupling can still be a very useful and convenient tool in the NMR armoury. It is very simple to set up, providing rapid answers to relatively simple questions, and can be particularly useful in identifying spins that share very small couplings that do not always reveal themselves in 2D correlation experiments. In very crowded spectra where only a specific interaction is to be investigated, the affected resonances may not be obvious and the use of difference spectroscopy can aid interpretation [2, 3]. Here, a control spectrum recorded in the absence of decoupling1 is subtracted from that collected in the presence of on-resonance decoupling to reveal any changes that arise. In such cases a 2D correlation experiment may, however, be more appropriate .One of the limitations to the use of selective decoupling lies in the

need to irradiate only a single resonance to identify the coupling partners of the desired target. Any saturation spillover onto neighbouring resonances introduces a degree of ambiguity into the interpretation.

Where the target multiplet is free from other resonances this posses little problem and the decoupler power can be set sufficiently high to ensure complete decoupling ($\gamma B_2 > J$ Hz). When other resonances are close in frequency to the target, it may be necessary to reduce the decoupler power and thus reduce the frequency spread to avoid disturbing neighbouring resonances. The penalty for reducing the decoupler power may be incomplete decoupling of the target spins, although changes within the fine structure of other resonances should be sufficient to identify coupled partners.
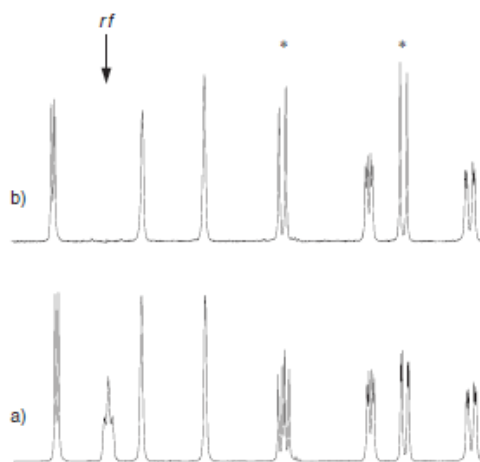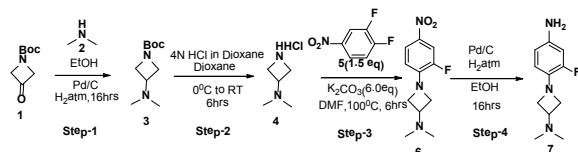

Figure 1. Homonuclear decoupling allows the rapid identification of coupled partners by removing couplings to the irradiated spin. (a) Control spectrum and (b) decoupled spectrum.

Bloch–Siegert shifts

The application of an rf field during the acquisition of the FID may also move signals that resonate close to the decoupler frequency. This effect is known as the Bloch–Siegert shift [4,5] and, more formally, it occurs when $\gamma B2$ becomes comparable to the shift difference in hertz between the decoupling frequency and the resonance. It arises because the decoupling field acts on the neighbouring spins such that they experience a modified effective field that is inversely dependent upon their resonance offsets from the decoupling frequency but proportional to $(\gamma B_2)^2$, which causes resonances to move away from this decoupling frequency (Fig. 2). The effect is principally limited to homonuclear

decoupling experiments, where resonances may be very close to the decoupling frequency, but is of no concern in most pulse NMR experiments since the rf pulse is turned off prior to data collection. A notable exception is when solvent presaturation is applied during the evolution time (t_1) of proton homonuclear 2D experiments. This can lead to shifts of f_1 frequencies of resonances close to the solvent, but since this is not present in f_2, it introduces asymmetry in the shifts of crosspeaks associated with these resonances. In homonuclear decoupling experiments it is rarely a major problem since the requirement for selectivity limits the B_2 field and thus keeps the shifts small. However, such small shifts may still introduce subtraction artefacts into decoupling difference spectra since the reference will not contain Bloch–Siegert shifts, so one should be cautious not to interpret these as evidence of coupling. Caution is also required should one need to measure accurate chemical shifts from decoupled spectra.

Synthesis and structure:

Scheme-1 Detailed scheme for the synthesis of 1-(2-fluoro-4-nitro-phenyl)-N,N-dimethylazetidin-3-amine {i.e. compound -6}
(1)after step-1 gave **(3)** which on treatment with TFA & DCM resulted in **(4)** after step-3 we obtained **(6)**, and **(6)** after step-4 resulted in (7) the compound under discussion.

^{1}H NMR spectra show δ value as (2H;7.93;m);(1H;6.55;t);(2H;4.20;d-d);(2H;3.95;dd);(1H;3.22;p);(6H;2.10;s)

The anomaly which is there in the ^{1}H NMR is the two doublet of doublet which are appearing at 4.20ppm and 3.95 ppm , because going by the rule of multiplicity we should get two doublet, but this doublet is again getting splitted into a doublet so two doublet of doublet. Homonuclear decoupling provided us with the solution of this problem.

The application of homonuclear irradiation whilst acquiring the FID poses some challenging instrumental problems. Whilst needing to detect the responses of the excited spins, one must not have the receiver open when the decoupler is on since this will simply swamp the NMR signal. The solution lies in the discrete sampling of the FID, and the application of homonuclear irradiation only when data points are not being sampled, that is, during the FID dwell time [6]. Spectrometers have purpose-built homonuclear decoupling modes to handle the necessary gating internally. The time in which the decoupler is gated on is thus only a small fraction of the total acquisition time, this so-called duty cycle typically being 20% or less. The low duty cycle means the effective mean decoupler power is somewhat less than the instantaneous B_2 field; hence rf powers are usually greater than those required for presaturation of a resonance where such receiver conflict does not arise. If the gating off of the decoupler is not perfect during data collection, a number of spectrum artefacts may be introduced [7,8]. Most notable are a reduction in signal-to-noise ratio, owing to 'leakage' of the decoupler rf into the receiver, and a significant 'spike' occurring at the decoupler frequency, although this is really only a question of aesthetics. The leakage problem varies greatly, it seems, from one instrument to another and if a serious problem may be cured by instrumental modification [8]. The second may be eliminated simply by setting the transmitter frequency to match that of the decoupler [9] so that the usual phasecycling routines employed in 1D acquisitions remove the unsightly 'zero-frequency' spike (Fig.2).

Figure-2 The aesthetically unappealing decoupler frequency 'spike' sometimes observed in homonuclear decoupling experiments as in (a) can be readily removed by setting the transmitter and decoupler frequencies to be the same, as in (b).
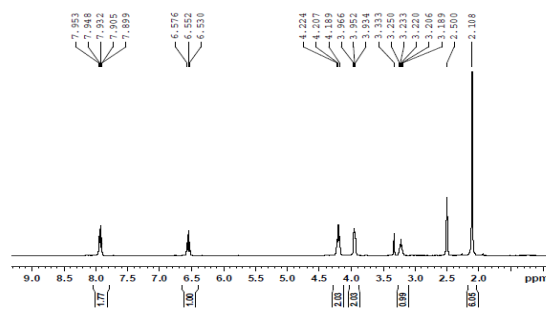
Results & Discussion :

Figure-3 Full view of NMR spectra of *1-(2-fluoro-4-nitrophe-nyl)-N,N-dimethylazetidin-3-amine* (source-Bruker AV 400)
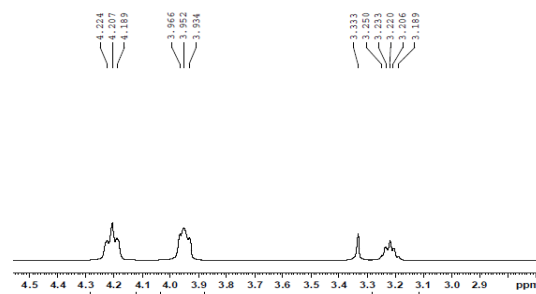
Figure-4 Expanded view of NMR spectra of *1-(2-fluoro-4-nitrophe-nyl)-N,N-dimethylazetidin-3-amine* (source-Bruker AV 400)
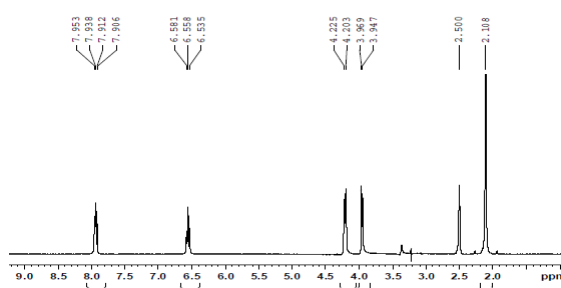
Figure-5 Full view of NMR spectra of *1-(2-fluoro-4-nitrophe-nyl)-N,N-dimethylazetidin-3-amine* (source-Bruker AV 400) with homonuclear decoupling .

From the studies conducted we concluded that axial and equatorial protons coupling with each other can be distinguished easily by homonuclear decoupling experiment the difference within the spectra is shown above.
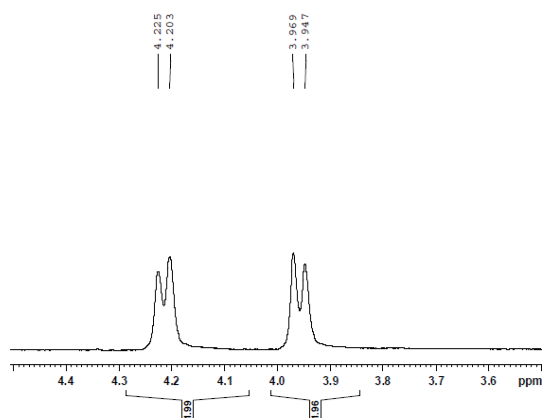
Figure-6 NMR spectra of *1-(2-fluoro-4-nitrophenyl)-N,N-dimethylazetidin-3-amine* (source-Bruker AV 400) showing two doublets as a result of decoupling .
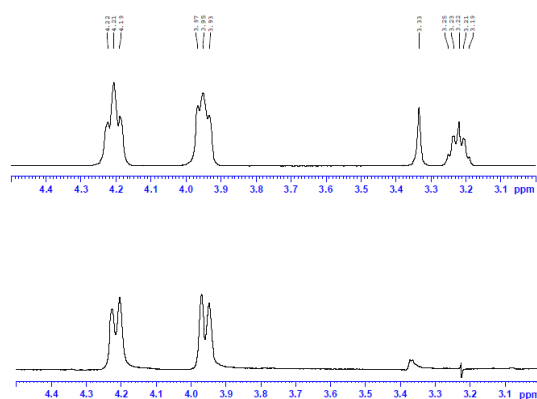
Figure-7 NMR spectra of *1-(2-fluoro-4-nitrophenyl)-N,N-dimethylazetidin-3-amine* (source-Bruker AV 400) showing difference after homonuclear decoupling.

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