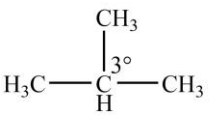
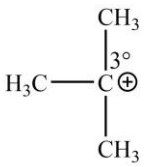
❖ Applications of NMR Spectroscopy in the Detection of Carbocations

Carbocations are the typical example of how the study of reaction intermediates is carried out. Two of the most popular and efficient experimental techniques to analyze the properties and structure of carbocationic species are ^{13}C and PMR (proton magnetic resonance) spectroscopy. The notable work in carbocation chemistry was carried out by George A. Olah, an American chemist who was also awarded the Nobel prize (1994) for the same.

Olah discovered that the NMR spectra of organic precursors in super-acid solutions were indicating relatively stable carbocations. He found that the chemical shifts (^{13}C NMR) of carbocations are much downfield than their parent compounds. For instance, the chemical shift for tertiary carbon in tert-butyl carbocation is at 330 ppm whereas the corresponding carbon in isobutane absorbs at 25.2 only. This can be explained in terms of reduced electron density at the carbon center in the carbonium ion.



δ = 25.2 ppm



δ = 330 ppm

^{13}C NMR in SO_2 ClF-SbF_5 Solution

The argument is also supported by other studies such as the NMR spectrum of substituted benzylic carbocations. More precisely, as the electron-withdrawing group becomes stronger at *p*-position in benzylic carbocation, the NMR peaks of cationic carbon shift towards the more down-field region.

Table 1. Benzylic carbocations' peaks in ^{13}C NMR spectra.

Substituents	δ(ppm)
p-OCH_3	219
p-CH_3	243
p-H	255
p-CF3	269

Now from Table 1, we might conclude that all electron-donating groups (like alky substituents) at carbonium center should behave in the opposite manner and should decrease the chemical shifts. Nevertheless, it is found that though the electron-donating alkyl groups directly attached to carbonium centers raise their stability, but little to no effect was found upon the chemical shift.

For instance, when CS_2 was taken as the reference standard, the chemical shift (^{13}C NMR) of secondary carbon in isopropyl carbonium ion appears at –125 δ whereas the tertiary carbon in tert-butyl carbocation shows the peak at –125 δ. Al this suggests that the replacement of hydrogen by methyl has actually supported the withdraw rather than the donation.

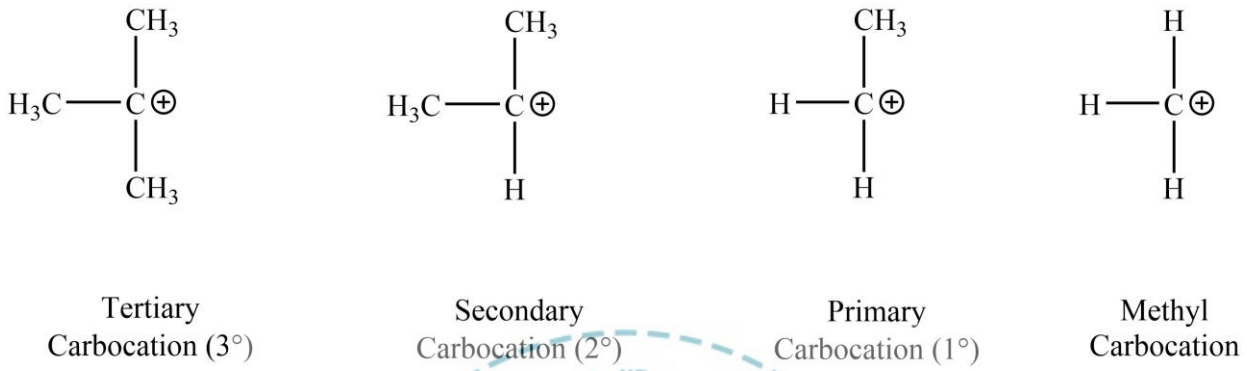
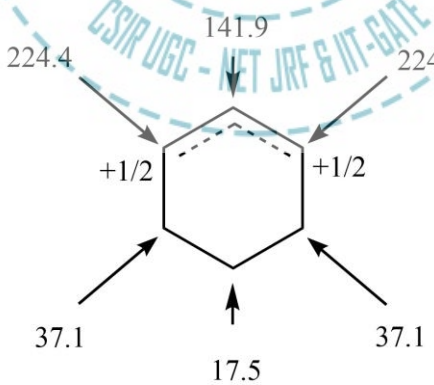


Figure 3. Some typical carbocations.

Furthermore, the molecular orbital theory also proves theoretically that the charges at 2° in isopropyl cation and 3° carbons in tert-butyl carbocations are +0.611 and +0.692, respectively.

Furthermore, the simplest arenium ion produced by the protonation of benzene ring strongly acidic solution can also be detected and studied by employing NMR spectroscopy. The chemical shifts for the o- and *p*- carbons (w.r.t protonation's site) in the ^{13}C NMR of arenium ion show very strong downfield movement which can be rationalized in terms of reduced electron density at the same.



A typical allylic cation with ^{13}CNMR spectrum

It is also worthy to note down from the Figure given above that the similar magnitudes of chemical shifts on the right and left side of carbocation suggest a plane of symmetry in the same.

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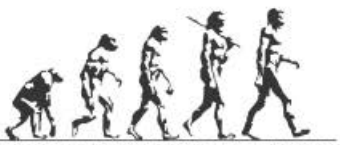

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