

- Applications of NOE :** (i) To establish the stereochemistry of some of the complex molecules ;
(ii) To study the *E* and *Z* isomers of alkenes ;
(iii) To determine interproton distances ;
(iv) To determine the structure of small molecules of protein in solution.

1.22 CARBON-13 NMR SPECTROSCOPY

Naturally occurring carbon is composed almost entirely of the carbon-12 isotope, which has no magnetic moment and thus is not detectable by NMR techniques. However, ^{13}C atoms, which make up about 1.1 percent of all carbon atoms, do absorb radio frequency waves in a manner similar to hydrogen. Thus, ^{13}C NMR is possible, and the technique provides valuable information about the structure of the carbon skeleton in organic molecules. Because, on an average only 1 out of every 100 carbon atoms in

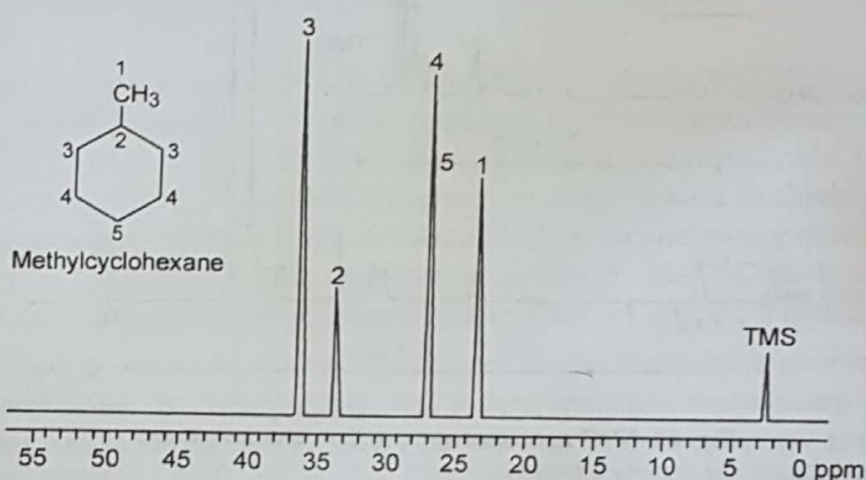


Fig. 47. The carbon-13 nuclear magnetic resonance spectrum of methylcyclohexane.

a molecule is a ^{13}C isotope and because ^{13}C atoms absorb electromagnetic radiation very weakly, ^{13}C NMR signals are about 6,000 times weaker than proton signals. Modern instrumentation has overcome this handicap, so that ^{13}C NMR is now a readily accessible analytical technique. The most important operational technique that has led to successful and routine ^{13}C NMR spectroscopy is the use *high-speed pulse technology coupled with broad-band heteronuclear decoupling of all protons*. As in proton spectra, the ^{13}C peaks are plotted as chemical shifts relative to an internal standard, such as the carbon resonance of tetramethylsilane (TMS). The spectrum of the cyclic hydrocarbon *methylcyclohexane* is shown as an example in Fig. 47. The chemical shifts of different carbon atoms are larger than for hydrogen atoms, and the five magnetically different ^{13}C atoms appear as five distinct peaks. As in proton spectra, the peak areas are proportional to the number of absorbing nuclei.

Thus, each of the peaks at 35.8 ppm and 26.8 ppm (generated by the two carbon atoms at the positions labeled 3 and 4, respectively, in the figure) have about twice the area of each of the peaks, at 23.1 ppm, 33.1 ppm, and 26.8 ppm (generated by the single carbon atoms at positions 1, 2, and 5, respectively). The two atoms labeled at position 3 are magnetically equivalent (as are the two at position 4), because the molecule is symmetrical about a line drawn vertically through its centre. The ^{13}C spectrum for methylcyclohexane does not show any multiplets arising from spin-spin splitting for two different reasons. The first reason is that spin-spin coupling between two adjacent ^{13}C atoms is so

weak that it does not show up on the spectrum. This is because nearly all the ^{13}C atoms in a molecule are bounded to more abundant ^{12}C atoms, which do not give rise to spin-spin splitting. The second reason is that the spin-spin splitting that does occur between ^{13}C atoms bounded to hydrogen atoms has been removed from the spectrum by an instrumental technique termed proton decoupling. Proton decoupling eliminates all the splitting patterns that would normally be observed in a ^{13}C spectrum for all carbon atoms bounded to one or more hydrogen atoms and is done routinely to simplify the spectrum.

Informations provided by carbon-13 NMR spectroscopy : (i) Provides informations regarding the carbon-skelton of molecule under examination.

- (ii) *Number of signals* indicate number of different carbons or different sets of equivalent carbons in the molecule under investigation.
- (iii) *Splitting of a signal* indicates the number of H-atoms attached to the carbon atom.
- (iv) *Chemical shift wrt TMS* provides information regarding the type of hybridization of the carbon atom. Carbon-13 chemical shift is nearly 20 times greater than that for protons.

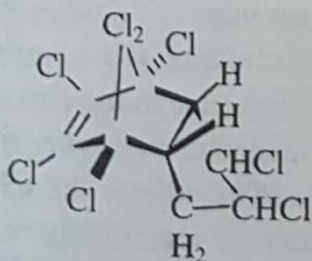
Type of hybridization	sp^3	sp^2	sp
Chemical shift (δ)	14-34	113-140	75-95

- (v) Provided information regarding the *electronic environment* of each carbon atom wrt other carbon atoms.

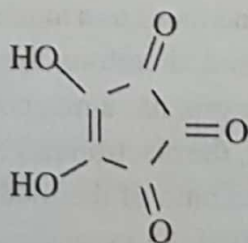
Notes : (i) Carbon NMR spectrum is *much simpler and more highly resolved* than proton NMR spectrum.

- (ii) The relative strength of carbon NMR, signals are not normally proportional to the number of atoms generating each signal.

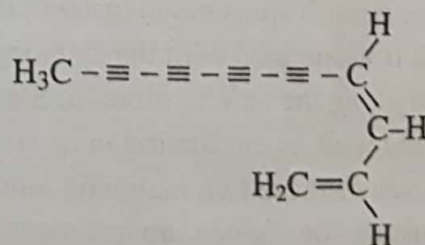
^{13}C NMR versus ^1H NMR spectroscopies. The power and usefulness of ^1H NMR spectroscopy as a tool for structural analysis has already been discussed. ^{13}C NMR is more complicated than ^1H NMR. ^{13}C NMR is much less sensitive to carbon as compared to ^1H NMR is to Hydrogen. Carbon NMR is Proton decoupled to prevent signal splitting as a result of J-coupling between Carbon and Hydrogen. Intensity of signal in ^{13}C NMR is not proportional to number of ^{13}C equivalent atoms unlike ^1H NMR. Unfortunately, when significant portions of a molecule lack C – H bonds, no information is forthcoming. Examples include polychlorinated compounds (*e.g.*, chlordane), polycarbonyl compounds (*e.g.*, croconic acid) and compounds incorporating triple bonds (*e.g.*, polyacetylene).



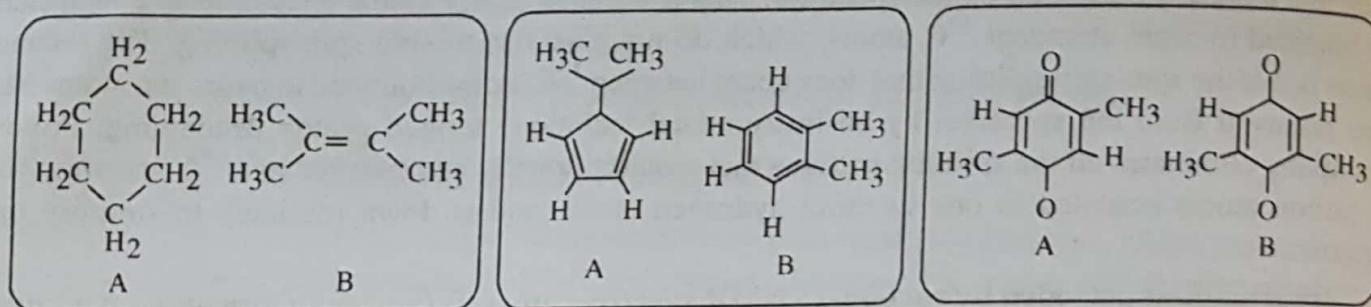
Chlordane



Croconic acid

A polyacetylene from *Dahlia*

Even when numerous C – H groups are present, an unambiguous interpretation of a proton NMR spectrum may not be possible. The following diagram depicts three pairs of isomers (A and B) which display *similar proton NMR spectra*.



The isomeric pairs previously cited as giving very similar proton NMR spectra are now seen to be distinguished by carbon NMR. In the example on the left box, cyclohexane and 2, 3-dimethyl-2-butene both give a single sharp resonance signal in the proton NMR spectrum (the former at δ 1.43 ppm and the latter at 1.64 ppm). However, in its carbon NMR spectrum, cyclohexane displays a *single signal* at δ 27.1 ppm, generated by the equivalent ring carbon atoms : whereas the isomeric alkene shows *two signals*, one at δ 20.4 ppm from the methyl carbons, and the other at 123.5 ppm (typical of sp^2 hybrid carbon atoms).

The C_8H_{10} isomers in the centre box have pairs of homotopic carbons and hydrogens, so symmetry should simplify their NMR spectra. The fulvene (isomer A) has five structurally different groups of carbon atoms and should display *five ^{13}C NMR signals* (one near 20 ppm and the other four greater than 100 ppm). Although ortho-xylene (isomer B) will have a proton NMR very similar to isomer A, it should only display *four ^{13}C NMR signals*, originating from the four different groups of carbon atoms. The methyl carbon signal will appear at high field (near 20 ppm), and the aromatic ring carbons will all give signals having $\delta > 100$ ppm.

Finally, the last isomeric pair, quinones A and B are easily distinguished by carbon NMR. Isomer A displays only *four carbon NMR signals* (δ 15.4, 133.4, 145.8 and 187.9 ppm); whereas, isomer B displays *five signals* (δ 15.9, 133.3, 145.8, 187.5 and 188.1 ppm), the additional signal coming from the non-identity of the two carbonyl carbon atoms.