

4.10 TYPES OF SPIN-SPIN COUPLINGS AND FACTORS AFFECTING THE COUPLING CONSTANTS

4.10.1 Geminal coupling constant (2J)

The coupling interaction between two non-equivalent protons on the same carbon atom is called geminal coupling and the coupling constant, designated as J_{gem} or $^2J_{\text{HH}}$, may be positive but more usually it has a negative sign. The general range is -20 to $+44$ Hz. Thus, the geminal protons exhibit the following ranges of J-values: terminal methylene groups, $^2J = 0$ – 3 Hz; in cyclopropane rings, $^2J = -4$ to -9 Hz; in cyclobutanes, $^2J = -7$ to -14 Hz; in cyclopentanes, $^2J = -10$ to -14 Hz and in cyclohexanes $^2J = -12$ to -14 Hz.

Factors affecting the geminal coupling constant

The variations in geminal coupling constants are conveniently explained in terms of the theoretical predictions of molecular orbital theory of coupling and may be summarized as follows:

4.10.1.1 DEPENDENCE OF GEMINAL COUPLING CONSTANT ON HYBRIDIZATION OF CARBON

The value of geminal coupling constant depends on the mode of hybridization (s-character of orbitals) of carbon bearing the protons. An increase in the H–C–H angle increases the s-character of the orbitals and makes the coupling more positive.

Table 4.8 *The systems in which it is possible to interpret the spin-spin splitting pattern of the NMR spectrum in a simple way, according to the (N + 1) rule, are summarized as follows:*

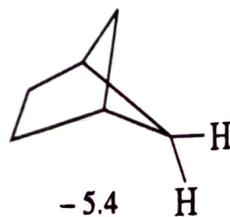
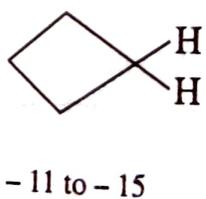
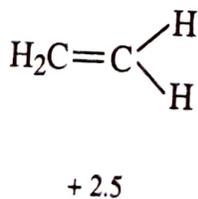
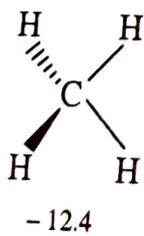
	Appearance of Resonance		
A. Spin System	A Resonance		
A	singlet		
A ₂	singlet		
A ₃	singlet		
A _n	singlet		
B. Spin System	A Resonance	X Resonance	
AX	1:1 doublet	1:1 doublet	
AX ₂	1:2:1 triplet	1:1 doublet	
AX ₃	1:3:3:1 quartet	1:1 doublet	
AX _n	(n + 1) memb. multiplet	1:1 doublet	
A ₂ X ₂	1:2:1 triplet	1:2:1 triplet	
A ₂ X ₃	1:3:3:1 quartet	1:2:1 triplet	
A ₂ X _n	(n + 1) memb. multiplet	1:2:1 triplet	
A _m X _n	(n + 1) memb. multiplet	(m + 1) memb. multiplet	
C. Spin System	A Resonance	M Resonance	X Resonance
AMX	pair of doublets	pair of doublets	pair of doublets
AMX ₂	pair of triplets	pair of triplets	pair of doublets
AMX ₃	pair of quartet	pair of quartet	pair of doublets

Table 4.9 Examples of various spin systems

S. No.	System containing two interacting nuclei	Examples
1.	A_2	$\text{Cl}-\text{CH}_2-\text{Cl}$; 1,1,2,2-tetrachloroethane
2.	AX	Dichloroacetaldehyde
3.	AB	2-Bromo-5-chlorothiophene
<i>Systems containing three interacting nuclei</i>		
4.	A_3	CH_3I , methylacetate contains two A_3 systems
5.	AX_2 or A_2X	1,1,2-Trichloroethane; 1,1,2,3,3-pentachloropropane
6.	AMX	Vinylacetate
7.	ABX	2,3-dichloropyridine
8.	ABC	Acrylonitrile, 3-nitro-o-xylene, 3-nitrosalicylic acid, 2,4-dinitrochlorobenzene
9.	AB_2 or A_2B	5-Nitro-m-xylene 1,2,4-trichlorobenzene 2,5-dichloronitrobenzene 2,6-dichloropyridine
<i>Four spin systems</i>		
10.	A_2X_2	Difluoromethane; phenylethylacetate
11.	A_2B_2	β -Chlorophenetole, β -iodopropionic acid, 2-chloroethanol
12.	$AA'XX'$	Difluoroethylene
13.	$AA'BB'$	<i>p</i> -Chloroaniline
<i>Systems containing five interacting nuclei</i>		
14.	A_2X_3	Ethyl group in ethyl acetate
15.	A_2B_3	Terminal ethyl group in <i>n</i> -hexyl bromide
16.	$ABB'MM'$	Bromobenzene

For example, the geminal coupling constant changes from -12.4 Hz in methane (sp^3 -hybridized methyl group) to $+2.5$ Hz in ethylene (sp^2 -hybridized methylene group). Cyclopropane, because of its special bonding character, has an intermediate value. The geminal coupling in cyclobutane is not much different from that in methane whereas other strained ring systems exhibit 2J values upto -5.0 Hz as depicted below.

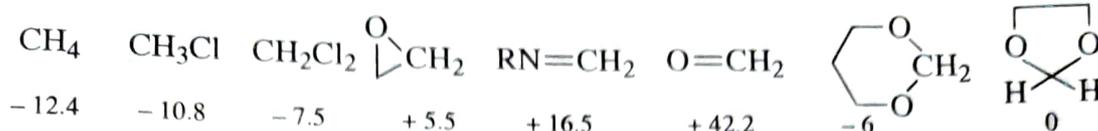
Dependence of 2J values on carbon hybridization



4.10.1.2 EFFECT OF SUBSTITUENTS

(i) The substitution of an electronegative atom in the α -position (i.e. an inductive effective) on sp^2 and sp^3 methylene groups leads to a positive change in the geminal coupling constant. In polysubstituted

methanes the effect of substituents, to a first approximation, is additive. The effect of electronegative substituent is shown below



The influence of oxygen in ethylene oxide results in a positive coupling constant for methylene hydrogen atoms. The especially large positive coupling constant in formaldehyde ($^2J = +42.2$ Hz) is due to the fact that the non-bonded electron pair on the oxygen atom has the correct symmetry for hyperconjugative donation. Thus, the reinforcement of the σ and π effects brings about the very large and positive coupling constant observed in formaldehyde. The lower electronegativity of nitrogen together with the less effective π overlap in imines decrease the effect ($^2J = 16.5$ Hz).

The steric orientation of non-bonded electron pairs relative to the orientation of C-H bonds under consideration is also of significance in the case of sp^3 -hybridized methylene groups. The comparison of 2J -values in 1,3-dioxane with those in the conformationally more rigid formaldehyde dioxolane illustrates this effect.

(ii) An electronegative β -substituent leads to a negative change in the value of the geminal coupling constant. An electropositive substituent, on the other hand, leads to a positive change in the magnitude of the coupling constant; the value varying from -3.2 Hz in vinyl fluoride to $+7.1$ Hz in vinyl lithium (Fig. 4.30).

(iii) π -Bonds adjacent to the methylene group in question exert a marked influence on the magnitude of geminal coupling constants. They cause a negative change i.e. the absolute value of the constants increases. Thus, the geminal coupling constant changes from 12.4 Hz in methane to 20.4 Hz in malononitrile (Fig. 4.30).

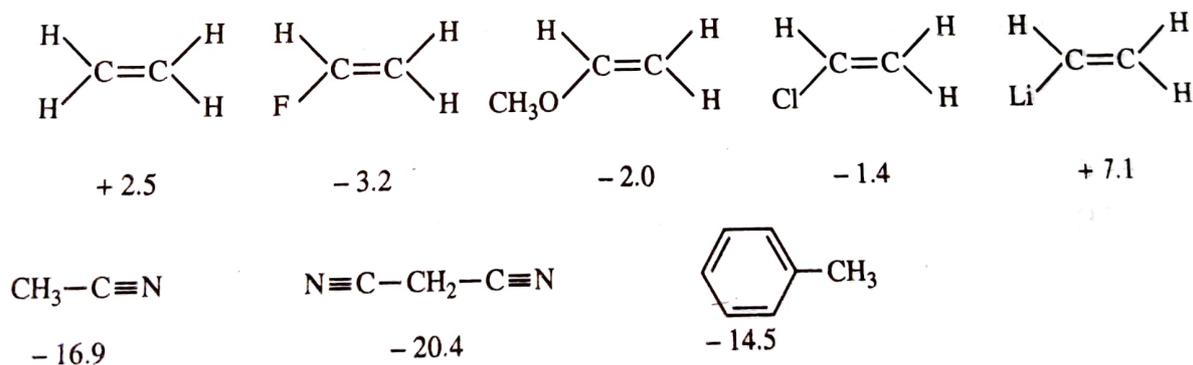


Fig. 4.30 The effect of substituent on geminal coupling constants.

(iv) A substituent which withdraws electrons from antisymmetric orbitals (i.e. hyperconjugative effects) gives a negative contribution.

The effect of hyperconjugative withdrawal of electrons is observed in allene, acetone and toluene. The result of this hyperconjugative electron withdrawal is a more negative geminal coupling, -9 Hz in the case of 1,1-dimethylallene, as illustrated in the (Fig. 4.31).

Most geminal couplings through a sp^2 carbon atom fall between the large positive value for formaldehyde and imines and the moderately negative value for allenes and ketenes.

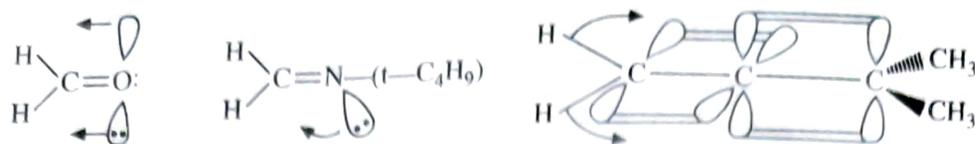


Fig. 4.31 Effect of hyperconjugative withdrawal of electrons on geminal coupling constants in formaldehyde, imine and 1,1-dimethylallene.

Table 4.10 Some geminal coupling constants (Hz)

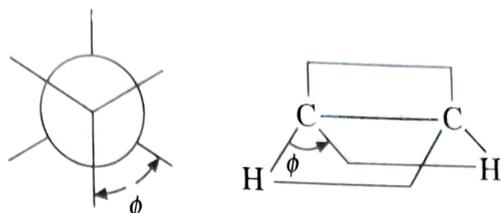
Compounds	Coupling constants
CH ₄	- 12.4
C ₆ H ₁₂	- 12.6
CH ₃ CCl ₃	- 13.0
C ₆ H ₅ CH ₃	- 14.4
	- 14.9
CH ₃ CN	- 16.9
BrCH ₂ CH ₂ CN	- 17.5
C ₆ H ₅ CH ₂ CN	- 18.5
CH ₂ (CN) ₂	- 20.3
CH ₃ OH	- 10.8
CH ₃ Cl	- 10.8
CH ₃ F	- 9.3
	- 9
	- 8.3
	- 6.0
H ₂ C=CHF	- 3.2
	0
H ₂ C=CH ₂	+ 2.5
H ₂ C=CH Li	+ 7.1
	+ 17
H ₂ C=O	+ 42.2

4.10.2 Vicinal coupling constant (3J)

Factors affecting the vicinal coupling constants

4.10.2.1 DIHEDRAL ANGLE BETWEEN TWO VICINAL C—H BONDS:

The coupling constant between two vicinal protons, $^3J_{HH}$ (the superscript 3 indicates the number of intervening bonds between the coupled nuclei) depends upon the dihedral angle ϕ between the two C—H bonds.



The relationship between dihedral angle ϕ and the vicinal coupling constant $^3J_{HH}$ is given by Karplus equation, the simplest form of which is represented by the following equation

$$^3J_{HH} = 8.5 \cos^2 \phi - 0.28 \quad (1)$$

The variation of vicinal coupling constant with the dihedral angle ϕ is represented graphically in the Fig. 4.32.

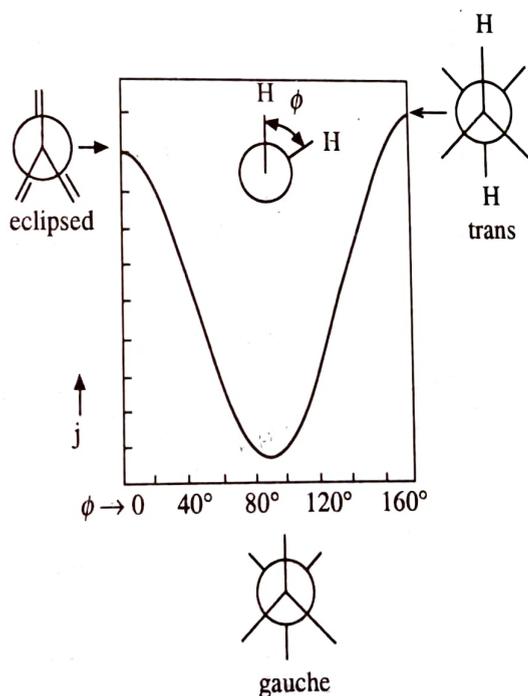
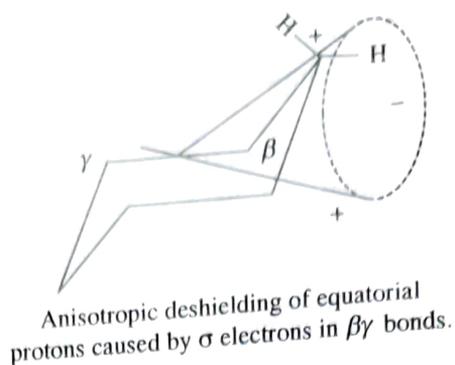


Fig. 4.32 Dependence of $^3J_{HH}$ on dihedral angle ϕ .

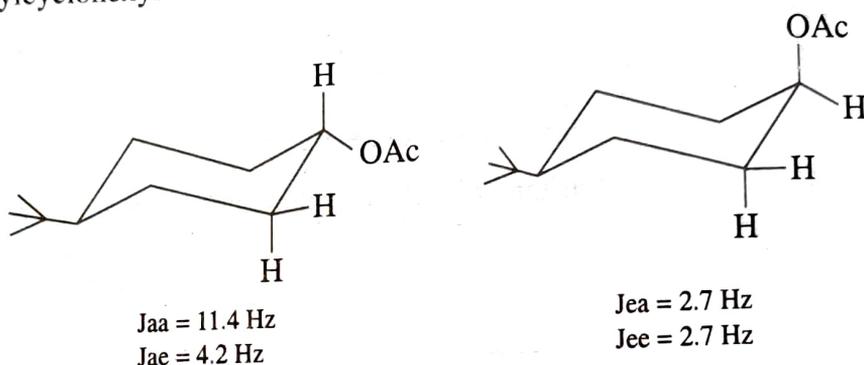
The value is at a maximum (~ 10 Hz) when ϕ is 180° (trans conformation) or 0° (eclipsed) and at a minimum (\sim zero), when ϕ is about 90° (gauche conformation).

The vicinal coupling constants for protons in cyclohexanes have been determined experimentally and also calculated using Karplus equation resulting in the following important generalizations:

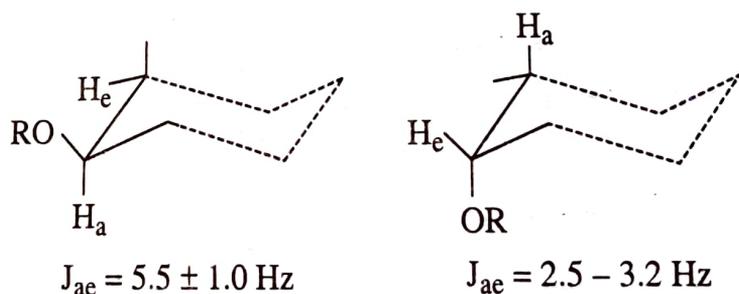
(i) In a saturated six-membered alicyclic ring, an equatorial proton resonates slightly downfield ($\Delta\delta = 0.4 - 0.5$ ppm) than the corresponding axial proton. This may be due to the anisotropic deshielding caused by the σ electrons in the $\beta\gamma$ bond as shown in the following Figure.



(ii) Diaxial protons display large coupling constant: $J_{a,a} = 8$ to 14 Hz (calculations: $\phi_{a,a} = 180^\circ$, $J_{a,a} = 11$ Hz according to Karplus equation) whereas axial-equatorial ($J_{a,e}$) or diequatorial ($J_{e,e}$) protons exhibit smaller coupling constants, usually 1 to 5 Hz (calculation: $\phi_{a,e} = 60^\circ$, $J_{ae} = 4$ Hz). For example, 4-t-butylcyclohexyl acetate shows the following coupling constants.



(iii) The gauche vicinal coupling constants in six-membered rings are dependent on the configurations. For example, the gauche coupling constants for a series of steroidal alcohols and their acetates are found to depend on the relative orientation of the C–O bonds, as shown below:



Sundaralingham³ suggested that this dependence on orientation (with respect to the ring) of the substituent on a ring carbon brings about small changes in the hybridization of that carbon.

(iv) In olefinic systems, the coupling of trans protons is always greater than that between cis protons.

(v) In the β -form of glucose, the anomeric proton possesses, in addition to higher shielding, a large vicinal coupling constant than in the α -form.

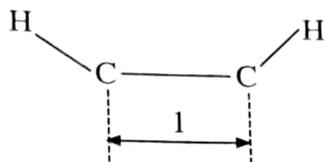
(vi) $^3J_{HH}$ in aromatic systems is quite large (6–10 Hz in benzene) because ortho protons have

3. M. Sundaralingham, J. Am. Chem. Soc. **87**, 599 (1965).

favourable dihedral angle (0°) and hence can be distinguished from J_{meta} ($1 - 3\text{Hz}$) and J_{para} ($0 - 1$ Hz).

4.10.2.2 (II) BOND LENGTH BETWEEN TWO VICINAL C—H BONDS

The vicinal coupling constants are very sensitive to small differences in the C—C bond length (l) and can give information regarding the degree of bond alternation in cyclic π systems, provided other factors are considered to be constant. Since the π bond order, $P_{\mu\nu}$, of MO theory correlates linearly



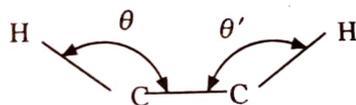
with the bond length, there also exists a linear relation for benzenoid aromatic compounds, between $P_{\mu\nu}$ and vicinal coupling constants as per the equation (9).

$${}^3J_{\text{HH}} = 12.47 (P_{\mu\nu}) - 0.71 \quad (9)$$

Thus, the length of the central C—C bond (single or double) is proportional to ${}^3J_{\text{HH}}$.

4.10.2.3 (III) VALENCE ANGLES BETWEEN C—H AND C—C BONDS

The dependence of vicinal coupling constants upon H—C—C valence angles is best described with the vicinal cis coupling constants across the double bond in cyclic mono olefins with different ring sizes (Table 4.11). Here a constant dihedral angle of 0° and the absence of substituent effects may be assumed.



The data in the Table 4.11 reveals that there is a steady increase in ${}^3J_{\text{cis}}$ in passing from cyclopropene to larger rings; the maximum value being observed in the eight-membered ring. Consequently a decrease in the valence H—C—C' and C—C'—H' in the fragment, H—C—C'—H' or H—C=C'—H' angles θ and θ' leads to an increase in the values of vicinal coupling constants.

Effect of electronegativity of substituents

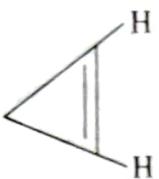
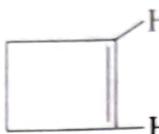
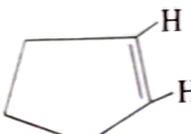
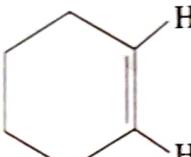
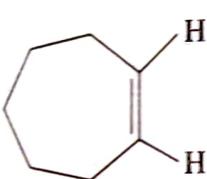
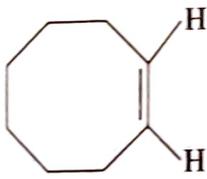
A decrease in the vicinal coupling is observed when an electronegative substituent is introduced at the H—C—C—H moiety in both saturated and unsaturated systems. For substituted ethanes, the relation between the vicinal coupling constant (${}^3J_{\text{HH}}$) and the electronegativity change, $\Delta E = E(X) - E(H)$, caused by the replacement of a hydrogen atom with a group X, is given by the equation (10).

$${}^3J_{\text{HH}} = 9.41 - 0.80 \Delta E \quad (10)$$

Similar relations (11) and (12) result for substituted ethylenes:

$${}^3J_{\text{trans}} = 19.0 - 3.3 \Delta E \quad (11)$$

Table 4.11 The dependence of vicinal coupling constants on the angles θ and θ'

Cyclic mono-olefins	${}^3J_{\text{HH}}$ (Hz)
	0.5–1.5
	2.5–3.7
	5.1–7.0
	8.8–11.3
	9.0–12.6
	10.0–13.0

$${}^3J_{\text{cis}} = 11.7 - 4.7 \Delta E \quad (12)$$

These effects are illustrated in the Table 4.12.

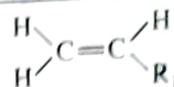
Effective nuclear charge

Since the Fermi contact mechanism for coupling between most common nuclei involves the pairing of electron and nuclear spins, it is, therefore, reasonable to assume that the magnitude of coupling should be a function of the amount of electron density at the nucleus. Furthermore the theoretical expression developed by Ramsay and Purcell⁴ involves the amount of *s*-electron density between the coupled nuclei, the magnitude of coupling should be related to the amount of *s*-electron density

4. N.F. Ramsay and E.M. Purcell, *Phys. Rev.* **85** (1952), 143.

Table 4.12 Effect of electronegativity of substituents on vicinal coupling constants in saturated and unsaturated systems

R	CH ₃ CH ₂ -R	³ J _{HH}	R ₁	³ J _{cis}	³ J _{trans}
Li		8.9	Li	19.8	23.9
SiR ₃		8.0	SiR ₃	14.7	20.4
CN		7.6	CH ₃	10.0	16.8
Cl		7.2	Cl	7.3	14.4
OCH ₂ CH ₃		7.0	F	4.7	12.8



between them. Grant and Litchman⁵ have reported that the coupling constant is proportional to the *s*-character (*S*) and the third power of the effective nuclear charge as per the following relation:

$$J \propto S Z^3$$

For example, the ¹³C-¹H coupling constant for CH₄ is 125 Hz, while that for CHCl₃ is 209 Hz. This difference may be due to the effective nuclear charge at the carbon. In CHCl₃ the electronegative chlorines remove the electron density from the carbon, thereby exposing more nuclear charge to the remaining electrons.

The dependence of coupling constant on effective nuclear charge for compounds that have approximately sp³ hybridisation at the carbon has been illustrated in the following Table 4.13.

Table 4.13 The dependence of effective nuclear charge on ¹J_{13C-1H}

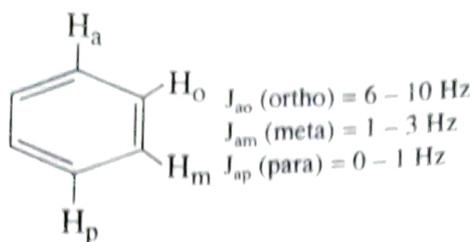
Compound	J (Hz)
CH ₄	125
(CH ₃) ₂ O	140
CH ₃ F	149
CH ₂ Cl ₂	178
CH ₂ F ₂	185
CHCl ₃	209
CHF ₃	238

Number of intervening bonds

The coupling constants are attenuated with increasing number of bonds separating the nuclei. This is illustrated by the following examples.

(i) The coupling constant for ortho coupled protons (³J_{ortho} = 6–10 Hz) is higher than that of the meta coupled protons (⁴J_{meta} = 1–3 Hz) which in turn is greater than that of the para coupled protons (⁵J_{para} = 0–1 Hz).

5. D.M. Grant and W.M. Litchman, J. Am. Chem. Soc., **87** (1965), 3994.



(ii) The general range for one bond $^{13}\text{C}-^1\text{H}$ coupling constants is from 100 to 250 Hz while the two bond $^{13}\text{C}-^1\text{H}$ couplings range from -10 to + 10 Hz.

Effect of hybridisation

When an element other than hydrogen is involved in the coupling, the coupling constant is proportional to the product of the amount of s character in the hybrid orbital used by each element in forming the bond. The following relation has been observed for a variety of one bond $^{13}\text{C}-^{13}\text{C}$ couplings.⁶

$$^1J(C_x - C_y) = 7.3 [(\% S_x)(\% S_y)/100] - 17$$

The equation predicts a value of 165 Hz for ethylene whereas the observed value is 157 Hz. The effect of hybridisation on one bond $^{13}\text{C}-^1\text{H}$ coupling constants is depicted in the Table 4.14.

Table 4.14 Effect of hybridisation on one bond $^{13}\text{C}-^1\text{H}$ coupling constant ($^1J_{^{13}\text{C}-^1\text{H}}$)

Compound	J (Hz)
CH_4	125
$\text{H}_2\text{C}=\text{CH}_2$	157
C_6H_6	159
$\text{HC}\equiv\text{CH}$	249

The percent s character is given by the relation, $\% s = 0.2 \ ^1J(^{13}\text{C} - ^1\text{H})$

For cubane $^1J(^{13}\text{C} - ^1\text{H}) = 160$ Hz

Therefore $\% s = 0.2 \times 160 = 32\%$

which corresponds to sp^2 hybridisation.

4.10.3 Long range coupling

The coupling through four or more bonds is often called long range coupling. The coupling constants are obviously quite small, the usual range is 0 - 3 Hz. Long range coupling occurs in the following types of systems:

4.10.3.1 LONG RANGE COUPLING IN π SYSTEMS

When a double or triple bond is one of the four intervening bonds, the coupling is called allylic coupling. Allylic coupling constants may range from 0.3 to 3 Hz.

H-C=C-CH	HC-C=C-CH	H-C≡C-CH
Allylic coupling	Homoallylic coupling	Allylic
($J = 0.3-3.0$ Hz)	($J = 0 - 1.5$ Hz)	($J = 2 - 3$ Hz)

Stereochemical requirements

Careful examination of the magnitude of allylic for a double bond incorporated in a ring clearly indicates that the value of J depends upon the extent of overlap of the carbon-hydrogen σ bond with the π bond. That is, allylic coupling is dependent upon stereochemical factors. This is well illustrated by taking the example of two structures (a) and (b) in Fig. 4.33, only the one in which the allylic carbon-hydrogen bond is axial, and therefore nearly parallel with the p -orbitals of the π bond, exhibits a doublet for the vinyl proton ($J = 1.5 - 2.00$ Hz).

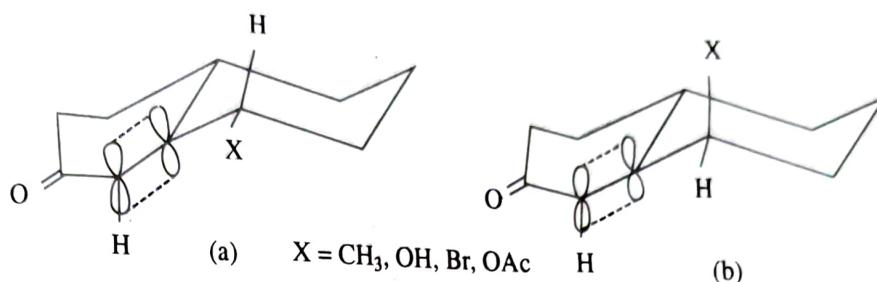


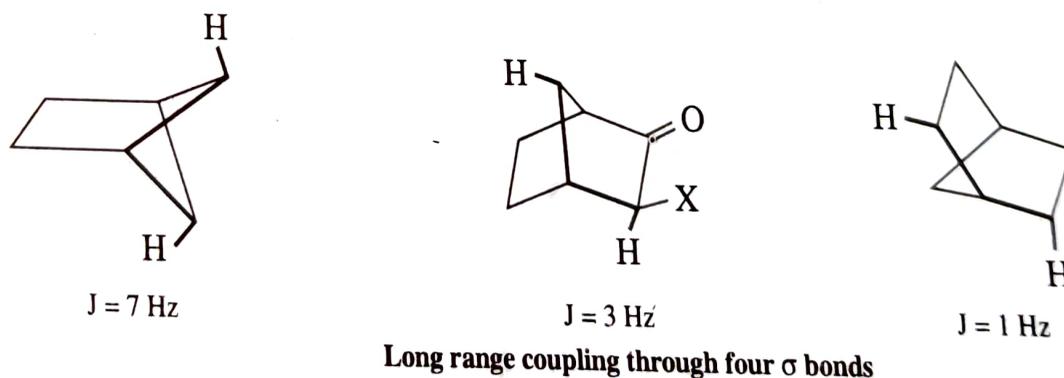
Fig. 4.33 Stereochemical requirements for allylic coupling (a) favourable (b) unfavourable.

Long range coupling has also been observed between two carbon-hydrogen groups separated by a double bond (homoallylic coupling) but the coupling constant is always less than 2 Hz and is difficult to observe.

4.10.3.2 LONG RANGE COUPLING THROUGH FOUR σ BONDS (W-COUPLING)

Long range coupling in completely saturated systems involves coupling through four σ bonds that are oriented in the form of W.

The W effect in saturated systems is well illustrated in cis and trans decalins.



Long range coupling through four σ bonds

The singlet pertaining to the angular 9-methyl group in the spectrum of 9-methyl-trans-decalin is broadened because of the long-range coupling to several protons as shown in the Fig. 4.34.

In 9-methyl-cis-decalin the methyl peak is a sharper singlet because only one W-arrangement of H-C-C-C-H is possible for methyl carbon-hydrogen bonds.