# Correlation of Interproton Spin–Spin Coupling Constants with Structure

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Since the advent of routine applications of high-resolution n.m.r. spectroscopy to structural determination in the late 1950s it has been realised[1] that the presence, or absence, of spin–spin splitting in n.m.r. resonances and the magnitude of the coupling constants involved, offer a powerful tool for structural investigations. The utilisation of spin–spin coupling constants for the determination of structure involves the solution of two separate problems, *viz.*, the determination of their magnitudes and the deduction of structural relationships from them. The first of these, that of *spectral analysis*, will not concern us here, but it is worth mentioning that the advent of n.m.r. spectrometers operating at ever higher magnetic fields and better resolution, and the routine utilisation of computer techniques, is making reliable spin–spin coupling data more easily available.

The amount of empirical data relating the characteristic magnitudes of spin–spin coupling constants (henceforth referred to as $J$ and measured in Hz) to structural features is very large, and much of it has been rationalised on a theoretical basis. It is the purpose of this Review to present the most important of these correlations. We shall restrict ourselves to the most commonly available group of coupling constants, the interproton coupling constants, and emphasise the less widely used correlations and the limitations of the more familiar ones.

Because terms like 'geminal coupling', 'long-range coupling', *etc.*, have become common usage, the material will be subdivided accordingly. It must, however, be emphasised that some of the classifications are based on convenience only and not on fundamental differences in the mechanisms involved. While contributions of major theoretical importance will be mentioned and some theoretical rationalisations of trends will be considered, a detailed discussion of the theory of spin–spin interactions will not be attempted.

It will be noted that in several examples discussed below we shall refer to coupling constants between equivalent protons, *e.g.*, the geminal coupling constants in methyl derivatives and vicinal coupling constants in symmetrically 1,2-disubstituted ethylenes. These data originate from either partially deuteriated compounds or from analyses of n.m.r. spectra based on $^{13}C$ satellites. In other cases, geminal coupling constants between the protons of a methylene group can be obtained because of the low symmetry of the molecule.

The vast majority of experimental data do not include the determination of the relative signs of coupling constants and, in particular, first-order analysis

[1] L. M. Jackman, 'Applications of n.m.r. spectroscopy in organic chemistry', Pergamon Press, Oxford, 1959, chap. 6.

gives only their absolute magnitudes. The concept is, however, necessary for the understanding of certain correlations, in particular with geminal and allylic coupling constants, either of which may take up values of comparable absolute magnitudes and opposite signs with changes of environment. For the present purposes it is sufficient to remember that a coupling constant of *positive* sign denotes (by convention) that the state where the coupled nuclei have opposed spins is of *lower* energy than the state with aligned spins.

Another fundamental concept which is pertinent to the present discussion is the time-dependence of the n.m.r. phenomena. In particular, coupling constants in molecules undergoing conformational changes at rates which are 'fast' on the n.m.r. time-scale (which is generally the case for spectra obtained at ambient temperatures) are *weighted averages* of the coupling constants in individual conformers. Where 'fast' intermolecular processes take place, *e.g.*, proton exchange in most alcohols and amines, the time of residence at each site permits the –OH or –NH protons to experience only the average magnetic environment thus effectively decoupling them from other magnetic nuclei. For this reason, techniques enabling us to reduce the rates of such processes, *e.g.*, the obtaining of the spectra of alcohols in dry dimethyl sulphoxide[2] or of amines in trifluoroacetic acid[3] permit us to observe the vicinal coupling $J_{H-O-C-H}$ (or $J_{H-N-C-H}$) and thus obtain additional structural information.

## 1 Geminal Coupling

We define geminal coupling as the spin–spin interaction between protons attached to the same atom. It is convenient to divide the discussion into three classes according to the type of central atom involved. Several compilations of data accompanied by discussion[4–7] and a number of theoretical papers[8–11] dealing with geminal coupling are available.

**A. Geminal Coupling across an $sp^3$ Hybridized Carbon Atom.**—It is often stated that coupling constants of this type 'generally take up values of $-12$ to $-18$ Hz' but in fact it can be seen (I—III) that a very much larger range of values can be found in quite common structures.[12] The principal influence is the nature of substituents attached to the methylene group and their orientation with respect

[2] O. L. Chapman and R. W. King, *J. Amer. Chem. Soc.*, 1964, **86**, 1256.

[3] W. R. Anderson and R. M. Silverstein, *Analyt. Chem.*, 1965, **37**, 1417.

[4] A. A. Bothner-By, in 'Advances in Magnetic Resonance', ed. J. S. Waugh, Academic Press, New York, 1965, vol. 1.

[5] R. J. Abraham, in 'Nuclear Magnetic Resonance for Organic Chemists', ed. D. W. Mathieson, Academic Press, New York, 1967.

[6] L. M. Jackman and S. Sternhell, 'Applications of n.m.r. spectroscopy in organic chemistry', Pergamon Press, Oxford, 1968, Part 4.

[7] R. C. Cookson, T. A. Crabb, J. J. Frankel, and J. Hudec, *Tetrahedron*, 1966, *Suppl.* **7**, 355.
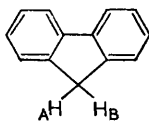
[8] J. A. Pople and A. A. Bothner-By, *J. Chem. Phys.*, 1965, **42**, 1339.

[9] M. Barfield and D. M. Grant, *J. Amer. Chem. Soc.*, 1963, **85**, 1899.

[10] M. Anteunis, *Bull. Soc. chim. belges*, 1966, **75**, 413.

[11] M. Barfield and D. M. Grant, in 'Advances in Magnetic Resonance', ed. J. S. Waugh, Academic Press, New York, 1965.
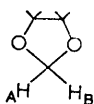
[12] K. L. Williamson, C. A. Lanford, and C. R. Nicholson, *J. Amer. Chem Soc.*, 1964, **86**, 762.
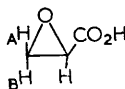
(I)

$J_{AB} = -22{\cdot}3$

(Ref. 7)

(II)

$J_{AB} = 0$ to $\pm 2$

(Ref. 6, 7)

(III)

$J_{AB} = +6{\cdot}3$

(Ref. 12)

to the two C–H bonds. The substituents with most pronounced influence are groups with $\pi$-bonds and heteroatoms, and theoretical rationalisation[7-11] of the observed trends is in terms of inductive electron withdrawal producing a positive increment (smaller negative values or larger positive values) and hyperconjugative electron withdrawal producing a negative increment. The efficiency of hyperconjugative electron shifts clearly depends on orientation.

The effect of a single $sp^2$ hybridized carbon substituent on $J_{gem}$ across an $sp^3$ carbon atom is illustrated in Figure 1 which is based on data of Cookson *et al.*[7] The range of values is in fair agreement with the calculations of Barfield and Grant[9] and it can be seen that, although a considerable spread exists, the values differ from the base value of $J_{gem}$ ($-12{\cdot}5$ Hz for either methane or cyclohexane) to an extent which makes the utilisation of this correlation for establishing of configuration or conformation attractive. In fact, although the curve in Figure 1 is extrapolated over a wider range of the projected angle $\theta$ than warranted by the experimental data,[7] there is little doubt about the general validity of the correlation which receives further support from the additive effect of further $sp^2$ hybridized carbon atoms. Thus, the very large geminal coupling constant in fluorene (I) is clearly due to the additive effect of two groups both of which are in the optimum configuration ($\theta = 30°$). The increment for a freely rotating $sp^2$ hybridized carbon atom is approximately $-1{\cdot}9$ Hz and a triple bond has the effect of two double bonds; thus $J_{gem}$ in acetonitrile is $-16{\cdot}9$ Hz and in malononitrile $-20{\cdot}3$ Hz.[9]

Electronegative substituents on the carbon atom carrying the geminal protons add positive increments to the coupling constants and, at least for freely rotating groups,[13] or for groups with identical orientations[14,15] the effects are approximately additive. The magnitude of the effects can be estimated from some typical[14-18] values (IV—VII) and, while the relationship with electronegativity is not straightforward in all cases, the general trend is clearly of considerable value in structure determination.

Smaller changes in the nature of $\alpha$-substituents may also be reflected in the

[13] R. A. Niedrich and D. M. Grant, *J. Chem. Phys.*, 1965, **42**, 3733.

[14] R. C. Cookson and T. A. Crabb, *Tetrahedron*, 1968, **24**, 2385.

[15] Y. Allingham, R. C. Cookson, and T. A. Crabb, *Tetrahedron*, 1968, **24**, 1989.

[16] H. J. Bernstein and N. Sheppard, *J. Chem. Phys.*, 1962, **37**, 3012.

[17] C. G. Macdonald, J. S. Shannon, and S. Sternhell, *Austral. J. Chem.*, 1966. **19**, 1527 and unpublished work from these laboratories with M. Lacey and A. Pross.

[18] T. Sato, Y. Saito, M. Kainosho, and K. Hata, *Bull. Chem. Soc. Japan*, 1967, **40**, 391.
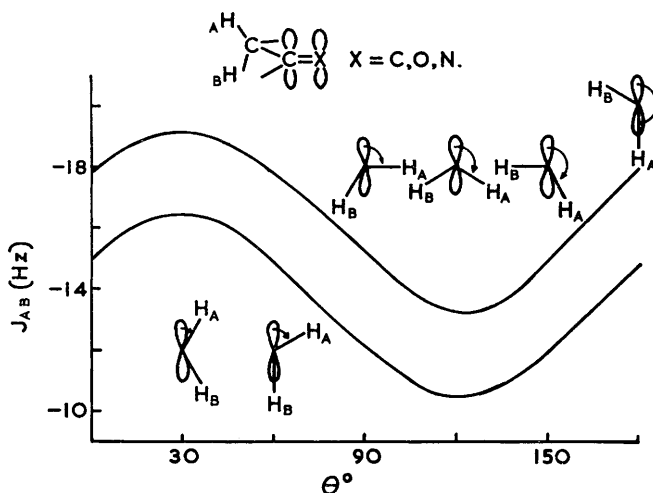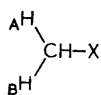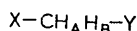
$$^A H \diagdown C=O$$
$$_B H \diagup C=X \quad X = C, O, N.$$

$H_B$ $H_A$  $H_A$ $H_B$  $H_B$ $H_A$  $H_B$ $H_A$

$H_A$  $H_A$
$H_B$  $H_B$

**Figure 1** *Effect of orientation of one sp²-hybridized adjacent carbon atom on $J_{gem}$ across an sp³-hybridized carbon atom.*

| | (IV) | | (V) | | | (VI) | | | (VII) | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $^A H$ ⟩CH–X $_B H$ | | X–CH$_A$H$_B$–Y | | | $^A H$ $H_B$ X⟨ ⟩Y | | | $^A H$ $H_B$ X⟨ ⟩Y | | |
| $J_{AB}$ | X | $J_{AB}$ | X | Y | $J_{AB}$ | X | Y | $J_{AB}$ | X | Y |
| −9·2 | I | −5·5 | Br | Br | −11·5 | O | CH$_2$ | −8 | O | CH$_2$ |
| −9·6 | F | −6·2 | Cl | Br | −6 | O | O | 0 | O | O |
| −10·2 | Br | −7·5 | Cl | Cl | −12 | N | CH$_2$ | −9·5 | N | CH$_2$ |
| −10·8 | U | −14·5 | CN | Br | −8·5 | N | N | −3·5 | N | N |
| −10·60 | OMe | −7·3 | OR | OR′ | −8 | N | O | −2·5 | N | O |
| −12·4 | H | | | | −13 | S | CH$_2$ | −10 | S | CH$_2$ |
| −14·1 | SiMe$_3$ | | | | −14 | S | S | −9·7 | S | S |
| −11·7 | NMe$_3$ | | | | −12·6 | CH$_2$ | CH$_2$ | | | |
| | (Ref. 16, 17) | | (Ref. 13, 18) | | | (Ref. 7, 14, 15) | | | (Ref. 14, 15) | |

magnitudes of the geminal coupling constants. Thus in *meta-* and *para*-substituted benzyloxytetrahydropyrans (VIII) the magnitude of the geminal coupling constants has an approximately linear relation[19,20] with Hammett substituent parameters. The sensitivity of $J_{gem}$ to this type of influence must be orientation-dependent, because in the corresponding substituted toluenes (IX)[21,22] the range of values is much smaller.
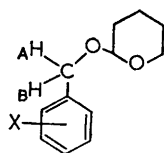
[19] R. R. Fraser, P. Hanbury, and C. Reyes-Zamora, *Canad. J. Chem.*, 1967, **45**, 2481.
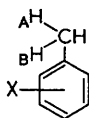[20] R. W. Franck and J. Auerbach, *Canad. J. Chem.*, 1967, **45**, 2489.
[21] C. G. MacDonald, J. S. Shannon, and S. Sternhell, *Austral. J. Chem.*, 1964, **17**, 38.
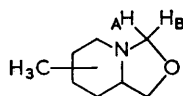[22] W. C. Ripka and D. E. Applequist, *J. Amer. Chem. Soc.*, 1967, **89**, 4035.

|   (VIII)   |        |   (IX)   |        |   (X)   |
|:----------:|:------:|:--------:|:------:|:-------:|

| $J_{AB}$ | X | $J_{AB}$ | X | $J_{AB} = -0.7$ to $-5.0$ |
|:--------:|:-:|:--------:|:-:|:-------------------------:|
| $-12.25$ | H | $-14.48$ | H | |
| $-11.31$ | $p$-NH$_2$ | $-14.93$ | $p$-NO$_2$ | |
| $-13.54$ | $p$-NO$_2$ | | | |

The orientation of α-substituents possessing lone pairs with respect to the methylene protons has a pronounced effect on the magnitude[7,10] of $J_{gem}$ as can be seen from the relative magnitudes of $J_{gem}$ in pairs of identically substituted (VI) and (VII). Studies by Anteunis[10] and by Cookson and Crabb and their collaborators[14,15] have led to the determination of the approximate magnitudes of 'eclipsing effects' for O, N, and S, which are the positive increments to $J_{gem}$ due to the eclipsing of the lone pairs with the C–H bonds of the methylene groups, and which amount to between +2 and +3 Hz. Clearly, considerable structural information is inherent in these correlations and several applications, *e.g.*, to the conformation[23,24] of the system (X) have appeared. The orientation-dependent effects are superimposed upon the positive increments due to the presence of electronegative substituents thus leading to very small values for $J_{gem}$ in some cases, *e.g.*, (VII) and (X).

In the absence of significant substituent effects it appears that geminal coupling constants in four-, five-, and six-membered rings do not differ greatly and are similar to those in acyclic compounds. Thus in all these systems one can *probably* assume a 'base value' of approximately $-12.5$ Hz. Surprisingly, $J_{gem}$ in cyclo-octane[25] is $-14.3$ Hz. However, in three-membered rings (XI) and with many strained bicyclic[26] and polycyclic systems, *e.g.*, (XII—XVI), $J_{gem}$ assumes more positive values, which can be of considerable diagnostic use, in particular in detection of three-membered rings.

Clearly, the positive values in epoxides and aziridines are due to a combination of rehybridization inherent in a three-membered ring, the presence of an electro-negative substituent, and the favourable orientation of the lone pairs on the heteroatom, all of which cause positive changes in $J_{gem}$.

[23] T. A. Crabb and R. F. Newton, *Chem. and Ind.*, 1966, 339.
[24] T. A. Crabb and R. F. Newton, *J. Heterocyclic Chem.*, 1966, **3**, 418; T. A. Crabb and R. O. Williams, *ibid.*, 1967, **4**, 169; T. A. Crabb and R. F. Newton, *Tetrahedron*, 1968, **24**, 2485; T. A. Crabb and R. F. Newton, *ibid.*, p. 1997; T. A. Crabb and R. F. Newton, *ibid.*, p. 4423; R. U. Lemieux, E. Fraga, and K. A. Watanabe, *Canad. J. Chem.*, 1968, **46**, 61.
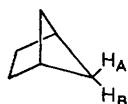[25] F. A. L. Anet and M. St. Jacques, *J. Amer. Chem. Soc.*, 1966, **88**, 2585.
[26] F. Kaplan, C. O. Schultz, D. Weisleder, and C. Klopfenstein, *J. Org. Chem.*, 1968, **33**, 1728.

(XI)

| $J_{AB}$ | X |
|---|---|
| $-0.5$ to $-9.1$ | C< |
| $+5$ | $^+$N< |
| $0$ to $+1$ | N– |
| $+4$ to $+6.3$ | O |
| $0$ to $-1.4$ | S |

(Ref. 7)
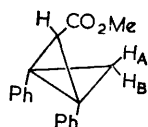
(XII)

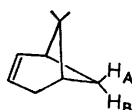$J_{AB} = -5.4$ to $-8.4$

(Ref. 7)

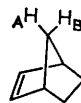(XIII)

$J_{AB} = -3.1$

(Ref. 7)



(XIV)

$J_{AB} = -1.7$

(Ref. 26)

(XV)

$J_{AB} = -9.1$

(Ref. 26)

(XVI)

$J_{AB} = -8$ to $-12$
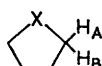
(Ref. 7)



(XVII)

| $J_{AB}$ | X |
|---|---|
| $-5$ to $-7.3$ | O |
| $-13.5$ to $-18$ | C=O |
| $-11$ to $-15$ | $CH_2$ |

(Ref. 7, 27)

(XVIII)

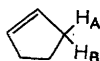| $J_{AB}$ | X |
|---|---|
| $-6.7$ to $-9.9$ | O |
| $-19$ to $-19.5$ | C = O |
| $-12$ to $-15$ | $CH_2$ |

(Ref. 7)

(XIX)

$J_{AB} = -12$ to $-14.6$

(Ref. 7, 28)
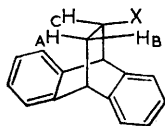


(XX)

$J_{AB} = -15.3$ to $-18.4$

(Ref. 7)

It is rather surprising that the geminal coupling constants in cyclobutanes are not more positive. In absence of results for cyclobutane and cyclopentane itself a reasonable estimate may be obtained by comparing groups (XVII)—(XX).[7,27,28]

[27] F. Nerdl and H. Kressin, *Annalen*, 1967, **707**, 1; M. Hara, Y. Odaira, and S. Tsutsumi, *Tetrahedron Letters*, 1967, 2981; R. J. Abraham, *J. Chem. Soc. (B)*, 1968, 173; L. H. Sutcliffe and S. M. Walker, *J. Phys. Chem.*, 1967, **71**, 1555.
[28] E. H. Hill and J. D. Roberts, *J. Amer. Chem. Soc.*, 1967, **89**, 2047.

If this approach is valid it can be deduced that there *is* a distinct trend towards more positive values in four-membered rings but that the effect is very much less pronounced than that in three-membered rings. It also appears that the effect is principally due to the different spatial relation between the C–H bonds and substituents in the ring in the cyclobutane derivatives, *i.e.*, it is likely that the H–C–H angle *per se* is not critical in this case.
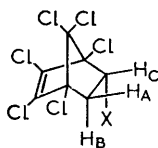
The influence of $\beta$-substituents on geminal coupling constants has been recognised. The values listed under structures[29-32] (XXI)—(XXV) are in each case the extremes for large series covering most of the commonly encountered substituents. In general, an increase in the electronegativity of the $\beta$-substituent is associated with a negative increment in $J_{gem}$ but the relationship is not simple and appears to depend on orientation.
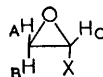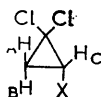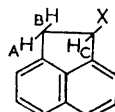


| (XXI) | | (XXII) | | (XXIII) | |
|---|---|---|---|---|---|
| $J_{AB}$ | X | $J_{AB}$ | X | $J_{AB}$ | X |
| $-12.3$ | $NH_2$ | $-12.6$ | CN | $+6.3$ | $CO_2H$ |
| $-14.2$ | $^+NMe_3$ | $-13.6$ | Cl | $+4.5$ | $OCOCH_3$ |
| (Ref. 29, 30) | | (Ref. 31) | | (Ref. 12) | |



| (XXIV) | | (XXV) | |
|---|---|---|---|
| $J_{AB}$ | X | $J_{AB}$ | X |
| $-4.9$ | $SiMe_3$ | $-19.0$ | $^+NMe_3$ |
| $-9.1$ | $OCOCH_3$ | $-17.1$ | $CH_2CO_2Me$ |
| (Ref. 12) | | (Ref. 32) | |

**B. Geminal Coupling across an $sp^2$ Hybridized Carbon Atom.**—Although this group of coupling constants is theoretically related to $J_{gem}$ across an $sp^3$ hybridized carbon atom, they are conveniently considered separately from the point of view of structural correlations because they are subject to different types of influence. It is often stated that coupling constants of this type 'generally take
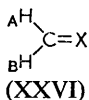
[29] S. J. Cristol, T. W. Russell, J. R. Mohrig, and D. E. Plorde, *J. Org. Chem.*, 1966, **31**, 581.
[30] Y. Terui, K. Aono, and K. Tori, *J. Amer. Chem. Soc.*, 1968, **90**, 1069.
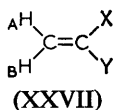[31] K. L. Williamson, *J. Amer. Chem. Soc.*, 1963, **85**, 516.
[32] C. K. Fay, J. Grutzner, L. F. Johnson, S. Sternhell, and P. W. Westerman, unpublished work.

up values of 1 to 3 Hz', but in fact it can be seen (XXVI—XXVIII) that a vastly larger range of values[33-37] can be found. Clearly, the values of $J_{gem}$ across an $sp^2$ hybridized carbon atom fall into three major groups: large positive values for formaldehyde derivatives, large negative values for cumulenes, and a range of values of either sign, including very small absolute values, for ethylene derivatives.



| $J_{AB}$ | X | | $J_{AB}$ | X | Y | | $J_{AB}$ | X |
|---|---|---|---|---|---|---|---|---|
| +42 | O | | +7·1 | H | Li | | −9·0 | CMe$_2$ |
| +17·5 to +7 | N–Y | | +2·5 | H | H | | −15·8 | O |
| (Ref. 4, 7, 8, 33) | | | +1·3 | H | CO$_2$H | | (Ref. 37) | |
| | | | 0 | H | NR$_2$ | | | |
| | | | −1·3 | H | Cl | | | |
| | | | −4·6 | F | F | | | |
| | | | (Ref. 4, 7, 8, 34, 35, 36) | | | | | |
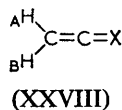
In ethylene derivatives, the magnitudes of $J_{gem}$ are related to the nature of the $\beta$-substituents (*i.e.*, X and Y in XXVII) and their effects are approximately additive. The relationship appears to be[36] of the form (1) where $E_X$ and $E_Y$ are

$$J_{gem} = \frac{61·6}{E_X + E_Y} - 12·9 \qquad (1)$$

the electronegatives[36] of the substituents X and Y in (XXVII), *i.e.*, $J_{gem}$ varies as the inverse of the sum of the electronegativities of the substituents. This is a contradiction of the *direct* relationship of the type (2) suggested earlier on the

$$J_{gem} = -a(E_X + E_Y) + b \qquad (2)$$

basis of a more limited set of data, and appears to necessitate further theoretical rationalisation. However, the very extensive tables of data for mono- and di-substituted ethylenes given in references 4, 7, 8, 34, 35, and 36, and the approximate additivity of the relationship, should enable the organic chemist to obtain reliable structural information from the magnitudes of $J_{gem}$. Further, examination of the plots of type (1)[36] and (2)[34] shows that the values of the constants are such that, with the usual range of substituents, $J_{gem}$ becomes more negative as the electronegativities of the substituents X and Y in (XXVII) increase.

[33] B. L. Shapiro, S. J. Ebersole, and R. M. Kopchik, *J. Mol. Spectroscopy*, 1962, **11**, 326; R. F. Curl, J. Hinze, D. F. Koster, and A. Danti, *ibid.*, 1967, **22**, 112.
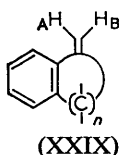[34] T. Schaefer, *Canad. J. Chem.*, 1962, **40**, 1.
[35] F. Hruska, G. Kotowych, and T. Schaefer, *Canad. J. Chem.*, 1965, **43**, 2827.
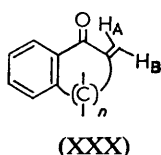[36] T. Schaefer and H. M. Hutton, *Canad. J. Chem.*, 1967, **45**, 3153.
[37] E. L. Allred, D. M. Grant, and W. Goodlett, *J. Amer. Chem. Soc.*, 1965, **87**, 673,
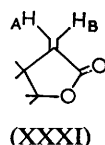
(XXIX)

| $\pm J_{AB}$ | $n$ |
|---|---|
| 0·5 | 1 |
| 0·5 | 2 |
| 1·4 | 3 |
| 1·5 α-methylstyrene | |
| (Ref. 38, 39) | |

(XXX)

| $\pm J_{AB}$ | $n$ |
|---|---|
| 0·95 | 1 |
| 2·05 | 2 |
| (Ref. 39) | |

(XXXI)

$J_{AB} = 0$ to $\pm 0·4$
(Ref. 39, 40)

(XXXII)

| $\pm J_{AB}$ | $n$ |
|---|---|
| $\geqslant 0·4$ | 3 |
| 2·26 | 4 |
| (Ref. 39) | |

(XXXIII)

$J_{AB} = \pm 3·6$
(Ref. 41)

(XXXIV)
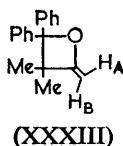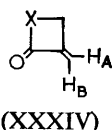
| $J_{AB}$ | X |
|---|---|
| $-3·87$ | O |
| $\pm 0·6$ | $CH_2$ |
| (Ref. 39, 42) | |

Comparison of $J_{gem}$ in exocyclic methylene groups[38–48] (XXIX—XL) with analogous 1,1-disubstituted ethylenes[4,7,8,34–36,38] suggests[6,39] that special effects associated with cyclic structures, perhaps related to substituent orientation or rehybridization through ring strain, operate. The rather wide range of $J_{gem}$ in a series of simple vinyl ethers[49] also suggests that the average orientation of substituents, as well as their nature, may be important. From the point of view of structural correlation it is also useful to note that undetectably small geminal couplings constants are by no means rare and appear to be characteristic of the commonly encountered fragment in (XXXI).

[28] A. W. Douglas and J. H. Goldstein, *J. Mol. Spectroscopy*, 1965, 16, 1; D. R. Davis and J. D. Roberts, *J. Amer. Chem. Soc.*, 1962, **84**, 2252.
[29] G. P. Newsoroff and S. Sternhell, unpublished work.
[40] D. Brookes, S. Sternhell, B. K. Tidd, and W. B. Turner, *Austral. J. Chem.*, 1965, **18**, 373.
[41] H. Gotthardt, R. Steinmetz, and G. S. Hammond, *J. Org. Chem.*, 1968, 33, 2774.
[42] F. Hruska, H. M. Hutton, and T. Schaefer, *Canad. J. Chem.*, 1965, **43**, 1942.
[43] K. R. Markham and I. D. Rae, *Austral. J. Chem.*, 1965, **18**, 1497.
[44] E. J. Mariconi and J. F. Kelly, *J. Amer. Chem. Soc.*, 1966, **88**, 3657.
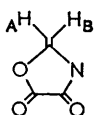[45] P. E. Butler and K. Griesbaum, *J. Org. Chem.*, 1968, 33, 1956.
[46] A. S. Atavin, A. N. Mirskova, and G. A. Kalabin, *J. Org. Chem. U.S.S.R.*, 1967, 3, 1737.
[47] M. Mühlstädt, M. Hermann, and A. Zschunke, *Tetrahedron*, 1968, 24, 1611.
[48] W. Rahman and H. G. Kuivilla, *J. Org. Chem.*, 1966, 31, 772; H. G. Peer and A. Schors, *Rec. Trav. chim.*, 1967, **86**, 161; E. Ciganek, *J. Amer. Chem. Soc.*, 1966, **88**, 1979.
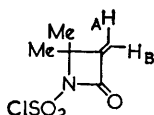[49] J. Feeney, A. Ledwith, and L. H. Sutcliffe, *J. Chem. Soc.*, 1962, 2021.
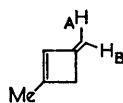
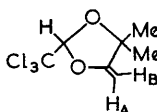(XXXV)

$J_{AB} = \pm 5$
(Ref. 43)

(XXXVI)

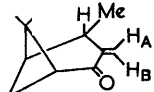$J_{AB} = \pm 2 \cdot 5$
(Ref. 44)

(XXXVII)

$J_{AB} = 0$
(Ref. 45)

(XXXVIII)

$J_{AB} = \pm 2 \cdot 7$
(Ref. 46)

(XXXIX)

$J_{AB} = -1 \cdot 7$
(Ref. 47)
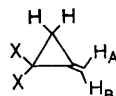
(XL)

| $\pm J_{AB}$ | X |
|---|---|
| 0·5 | Br |
| 0·7 | Cl |
| 2·2 | CN |

(Ref. 48)

**C. Geminal Coupling across a Heteroatom.**—This type of coupling is rarely encountered but a number of values are available in the literature. Thus $J_{\text{H-P-H}}$ = 10—12 Hz,[50,51] $J_{\text{H-S-H}}$ = 13·7 Hz,[52] $J_{\text{H-Si-H}}$ = +2·8 to +11·3 Hz, $J_{\text{H-Ge-H}}$ = +7·69 to +12·4 Hz, and $J_{\text{H-Sn-H}}$ = +15·3 to +20·2 Hz.[53] Interestingly, in some amides $J_{\text{H-N(COR)-H}}$ is in the range of 2·2—2·5 Hz,[54] possibly reflecting the $sp^2$-like hybridization of the nitrogen atom.

**2 Vicinal Coupling**
We define vicinal coupling as the spin–spin interaction between protons attached to contiguous atoms, *i.e.*, across three bonds. Clearly, the majority of vicinal coupling constants of interest in structural determination concern the systems H–C–C–H and H–C=C–H and it will be convenient to discuss them principally under these headings, although the two types of interaction are believed to involve similar mechanisms.[55] We shall defer the discussion of vicinal coupling in aromatic and heterocyclic systems to a separate section.

**A. Vicinal Coupling in the System H–C–C–H (both Carbons $sp^3$ Hybridized).**—A number of recent discussions[4-8] and one major compilation of data[4] are available in this area. The most useful summaries of the theoretical background are due

[50] S. L. Manatt, G. L. Juvinal, and D. D. Elleman, *J. Amer. Chem. Soc.*, 1963, **85**, 2664.
[51] H. Goldwhite and D. G. Rowsell, *J. Phys. Chem.*, 1968, **72**, 2666.
[52] H. Schmidbauer and W. Siebert, *Z. Naturforsch.*, 1965, **20b**, 596.
[53] H. Dreeskamp and C. Schumann, *Chem. Phys. Letters*, 1968, **1**, 555.
[54] H. Kamei, *Bull. Chem. Soc. Japan*, 1965, **38**, 1212.
[55] M. Karplus, *J. Chem. Phys.*, 1959, **30**, 11.

to Karplus,[56] Bothner-By,[4] and to Barfield and Grant,[11] but at present many of the details, especially the dependence of $J_{vic}$ on the nature and orientation of substituents, must be considered in an essentially empirical manner.[6,10,12,31,32,57–63]

Vicinal coupling constants in saturated systems take up values of $-0.3$ to $+14$ Hz and the dominant influence on the magnitude of $J_{AB}$ in the system $H_A$–C–C–$H_B$ is the dihedral angle $\phi$ between $H_A$ and $H_B$, defined in the Newman projection in Figure 2. The angular dependence is believed to take the form of the well known Karplus relation[55,56] generally expressed as (3) where $J^0$, $J^{180}$,

$$\left. \begin{array}{l} J = J^0 \quad \cos^2\phi \ - \ C \text{ for } \ 0° \leqslant \phi \leqslant \ 90° \\ J = J^{180} \cos^2\phi \ - \ C \text{ for } 90° \leqslant \phi \leqslant 180° \end{array} \right\} \tag{3}$$

and $C$ are constants. The original calculations by Karplus[55] predicted the values of $J^0 = 8.5$ Hz, $J^{180} = 9.5$ Hz, and $C = -0.3$ Hz for an unsubstituted ethanic fragment. According to later calculations[56] a more appropriate form of equation (3) can be derived, but this gives results so similar numerically that no practical advantage accrues from its use in view of the much larger uncertainties introduced by other *structural* factors (see below). The present situation may be summarized[5,6] as follows: It is believed that the general *form* of the Karplus relation is correct, but that the values of $J^0$ and $J^{180}$ appropriate for specific systems may vary from 8 to 16 Hz with $J^{180}$ generally larger. It is found empirically that the values of $J_{vic}$ for $\phi = 90°$ are very small and thus, in view of other uncertainties, it is probably quite safe to ignore the constant $C$ in straightforward applications in organic chemistry. The quantitative application of the Karplus relation thus reduces to consulting a family of curves shown in Figure 2 after choosing a complete 'Karplus curve' composed of two segments, *e.g.*, those labelled 'a' and 'b' in Figure 2. It might appear that, in view of the wide range of values of $J^0$ and $J^{180}$, and of other factors enumerated below, the applicability of the Karplus relation to structural problems is limited. This is, however, not correct, because, while it is undoubtedly quite unsound to derive the absolute magnitudes of dihedral angles to better than *ca.* $\pm 5°$, even in favourable circumstances, it *is* possible to solve the vast majority of pertinent structural and conformational problems by the use of the Karplus relation in conjunction with Dreiding models. This is the case because the choice of values of $J^0$ and $J^{180}$ is very rarely critical in 'fitting' the experimentally obtained vicinal coupling constants to the various stereochemical options.

The following procedure is suggested: The Dreiding models of all reasonable configurations and conformations should be constructed and the relevant dihedral angles should be measured, compensating for likely conformational

[56] M. Karplus, *J. Amer. Chem. Soc.*, 1963, **85**, 2870.
[57] E. W. Garbisch, *J. Amer. Chem. Soc.*, 1964, **86**, 5561.
[58] A. D. Cohen and T. Schaefer, *Mol. Phys.*, 1966, **10**, 209.
[59] H. Booth, *Tetrahedron Letters*, 1965, 411.
[60] H. Booth and P. R. Thornburrow, *Chem. and Ind.*, 1968, 685.
[61] R. J. Abraham and W. A. Thomas, *Chem. Comm.*, 1965, 431.
[62] S. Wolfe and J. R. Campbell, *Chem. Comm.*, 1967, 872.
[63] P. Laszlo, Thesis, Paris 1965; P. Laszlo and P. R. Schleyer, *Bull. Soc. chim. France*, 1964, 87.
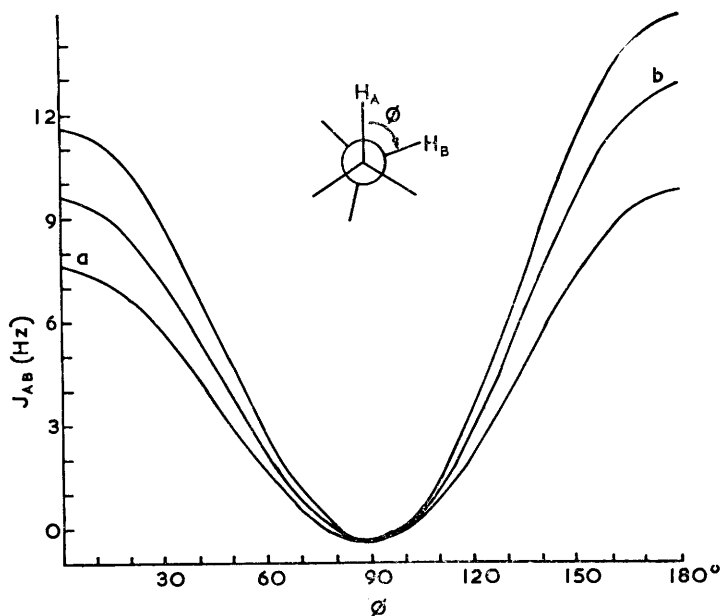
**Figure 2** *Plot of the 'Karplus relation' for selected values of $J^{0}$ and $J^{180}$ (see equation 3).*

distortions by obtaining ranges of angles. The 'theoretical' vicinal coupling constants for each of the options should then be obtained by consulting a graph of the type shown in Figure 2 or performing the relevant arithmetic for *two* sets of $J^{0}$ and $J^{180}$ considered likely to be extreme for the structure under consideration. In presence of no more than one strongly electronegative substituent an (arbitrary) appropriate set of extreme values might be $J^{0} = 8$ with $J^{180} = 12$ and $J^{0} = 12$ with $J^{180} = 16$ Hz. It will be found that, in the great majority of instances, only one set of 'theoretical' vicinal coupling constants (fortunately most problems either involve more than one vicinal coupling constant or are trivially simple) can be fitted to the experimentally obtained vicinal coupling constants without producing at least one *gross* discrepancy.

This procedure is most appropriate to systems where no large angular distortion is present and which are believed to be conformationally pure. Problems involving four- and five-membered rings, unless definitely 'locked' into rigid (but not grossly distorted) structures, require most care, principally in choosing the values of $\phi$ from models, but can generally be satisfactorily settled. The, necessarily rigid, three-membered rings present least difficulty, $J_{cis}$ always being larger than $J_{trans}$ and only corrections due to presence of electronegative substituents or heteroatoms need to be chosen (see below). Highly strained systems can be analysed only by reference to related systems.

In flexible systems with relatively small energy differences between conformers the problem involves the estimation of proportions of conformers from the

values of the averaged vicinal coupling constants and a different approach must be used. First, a choice of fixed structures, believed to be appropriate models for the conformers contributing to the mixture must be made. From the remarks made in the introductory section, it follows that the averaged $J_{vic}$ can then be simply related to the proportion of individual conformers in the rapidly inter-converting mixture of conformers. Obviously, the most reliable data involve systems where only two conformers are believed to be present. Extensive investigations in the cyclohexane series have been reported;[64,65] for particularly clear expositions, the reader is referred to the investigations of the conformations of cyclohexanol and cyclohexyl acetate[66] and of 2-bromocyclohexanone.[67] Acyclic systems (*i.e.*, ethanic fragments) present more difficulties because of scarcity of suitable models and because in structures of low symmetry more than two conformers must be considered. Nevertheless, quite far-reaching conclusions can often be reached even with the latter systems[68] and the extremely common problem of differentiation between *threo*- and *erythro*-isomers can often be solved by consideration of the relative magnitudes of vicinal coupling constants.[69]

On theoretical grounds[56] it is expected that an increase in the magnitudes of the angles H–C–C′ and C–C′–H′ should decrease the size of the vicinal coupling constants in the fragment H–C–C′–H′. This effect appears to be very significant in the system H–C=C–H (see below) but can *probably* be ignored in solving structural problems involving simple saturated carbocyclic systems on the following evidence: while it is difficult to obtain empirical Karplus curves for rings of various sizes, it is possible to compare one point, *viz.*, that corresponding to $\phi = 0°$. It has been recently established[70] that for cyclopropane itself, $J_{cis} = +9.5$ Hz, which is not significantly smaller than $J_{cis}$ in, *e.g.*, acenaphthene and hexachlorobicyclo[2,2,1]heptene (see Table 1). Thus, if the above angular dependence is indeed important in saturated systems, it is numerically less significant than the effects of quite common substituents (see below). Highly strained polycyclic systems must, however, always be considered only by comparison with closely related systems.

The above does not, of course, signify that characteristic ranges of vicinal coupling constants are not associated with definite stereochemical relations in cyclic compounds. Thus, in the chair form of cyclohexane derivatives the values of $J_{trans:\ axial,\ axial}$ range upward from 8 Hz while $J_{trans:\ equatorial,\ equatorial}$ and $J_{cis:\ axial,\ equatorial}$ are always below 6 Hz. Similarly, while in cyclopro-

[64] E. L. Eliel, *Angew. Chem. Internat. Edn.*, 1965, **4**, 761.
[65] N. C. Franklin and H. Feltkamp, *Angew. Chem. Internat. Edn.*, 1965, **4**, 774.
[66] F. A. L. Anet, *J. Amer. Chem. Soc.*, 1962, **84**, 1053.
[67] E. W. Garbisch, *J. Amer. Chem. Soc.*, 1964, **86**, 1780.
[68] L. M. Jackman and N. S. Bowman, *J. Amer. Chem. Soc.*, 1966, **88**, 5565; M. Buza and E. I. Snyder, *ibid.*, p. 1161.
[69] J. C. Randall, R. L. Vaulx, M. E. Hobbs, and C. R. Hauser, *J. Org. Chem.*, 1965, **30**, 2035; C. A. Kingsbury and W. B. Thornton, *J. Amer. Chem. Soc.*, 1966, **88**, 3159; C. A. Kingsbury and W. B. Thornton, *J. Org. Chem.*, 1966, **31**, 1000; C. A. Kingsbury and D. C. Best, *ibid.*, 1967, **32**, 6; C. A. Kingsbury, *ibid.*, 1968, **33**, 1128; G. P. Newsoroff and S. Sternhell, *Austral. J. Chem.*, 1968, **21**, 747; L. E. Erickson, *J. Amer. Chem. Soc.*, 1965, **87**, 1867.
[70] S. Meiboom and L. C. Snyder, *J. Amer. Chem. Soc.*, 1967, **89**, 1038.

pane derivatives[4-6] the ranges of vicinal coupling constants overlap ($J_{cis}$ 6·6—12·5 Hz and $J_{trans}$ 3·9—8·6 Hz), unequivocal stereochemical decisions can be made if the effect of the substituents is considered (see below). For four-[4,5,6,71-76] and five-membered[4,5,6,61] rings the *cis* and *trans* vicinal coupling constants are not associated with characteristic ranges and each problem must be analysed separately in the light of the Karplus relation and substituent effects (see below). This is clearly due to the relative flexibility of these systems, and in four- and five-membered rings approaching planarity $J_{cis}$ is generally significantly larger than $J_{trans}$, as expected from the Karplus relation, and exemplified in structures (XLI)—(XLV) and in data quoted in Table 1. An exception has, however, been noted for a series of dihydrobenzofurans.[72] The introduction of a double bond into a five-membered ring generally has little effect on the vicinal coupling constants[6,61] in the fully saturated fragment, but in cyclobutene[28] $J_{cis} = 4·65$ and $J_{trans} = 1·75$ Hz, while in cyclobutane[70] $J_{cis} = 10·4$ and $J_{trans} = 4·9$ Hz.
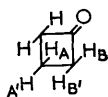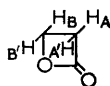


(XLI)

$J_{AB} = +10·0$,    $J_{AB'} = +6·4$
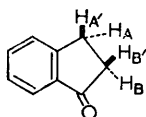$J_{AA'} = -11·1$,    $J_{BB'} = -17·5$
(Ref. 73)

(XLII)

$J_{AB} = +6·93$,    $J_{AB'} = +4·61$
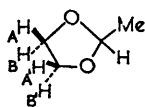$J_{AA'} = -16·40$,    $J_{BB'} = -5·00$
(Ref. 74)

(XLIII)

$J_{AB} = 8·65$, $J_{AB'} = 3·49$
(Ref. 75)
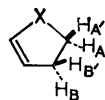
(XLIV)

$J_{AA'} = 7·1$, $J_{AB'} = 6·0$
(Ref. 76)

(XLV)

| $J_{AB}$ | $J_{AB'}$ | X |
|---|---|---|
| 7·4 | 4·6 | $CH_2$ |
| 7·2 | 2·2 | C=O |
| 10·7 | 8·3 | O |
| 10·0 | 7·5 | S |

(Ref. 5)

[71] H. Weitkamp and F. Korte, *Tetrahedron*, 1966, *Suppl.* 7, 75; K. D. Bartle, R. L. Edwards, D. W. Jones and I. Mir, *J. Chem. Soc.* (C), 1967, 413; I. Fleming and D. H. Williams, *Tetrahedron*, 1967, 23, 2747; J. Krepinsky, Z. Samek, F. Šorm, D. Lamparsky, P. Ochsner, and Y. R. Naves, *Tetrahedron*, 1966, *Suppl.* 8, Part 1, 53.
[72] L. H. Zalkow and M. Ghosal, *Chem. Comm.*, 1967, 922.
[73] L. H. Sutcliffe and S. M. Walker, *J. Phys. Chem.*, 1967, 71, 1555.
[74] R. J. Abraham, *J. Chem. Soc.* (B), 1968, 173.
[75] S. Forsen, B. Gestblom, R. A. Hoffman, and S. Rodmar, *J. Mol. Spectroscopy*, 1966, 21, 372.
[76] R. J. Abraham, *J. Chem. Soc.*, 1965, 256.

The effect of substituents on the magnitude of vicinal coupling constants has been widely recognised[77] and in systems where the stereochemistry remains approximately constant, electronegative substituents at C(1) or C(2) in the fragment $H_A$–C(1)–C(2)–$H_B$ tend to lower the value of $J_{AB}$ (Table 1). Further, as seen in, *e.g.*, the comparison of values in columns 1 and 2 of Table 1, the effect is approximately additive. At least over limited ranges of Dailey electronegativity[78] the relationship appears to be approximately linear, *i.e.*, of the form given in equation (2),[12,29,31,32,77,79] with the values of the constants $a$ and $b$ characteristic for each system. In view of the approximate nature of this correlation, its rather complicated dependence upon the orientation of the substituents, the possibility of distortion[62] in most systems and of the recently demonstrated breakdown[36] of a similar correlation in ethylenic fragments, the theoretical picture must be regarded as uncertain, but the definite trends shown in Table 1 can be of considerable value in the determination of structures of organic compounds, and should be taken into consideration in conjunction with any attempt to utilise the Karplus relation.

**Table 1** *Effect of substituents on vicinal coupling constants*[a]

| CH₃–CH₂–X (Ref. 4) | | X–C'H₂–C'H₂–Y (Ref. 77) | | | (XXI) (Ref. 31) | | |
|---|---|---|---|---|---|---|---|
| $J(CH_3,CH_2)$[b] | X | $J(CH_2,C'H_2)$[b] | X | Y | $J_{AC}$ | $J_{BC}$ | X |
| 8·90 | Li | 6·83 | Cl | Cl | 9·5 | 3·0 | NH₂ |
| 8·0 | H | 5·83 | Cl | OH | 9·0 | 3·5 | Tos |
| 7·23 | Cl | 6·80 | CH₃CO | CO₂Me | 8·0 | 2·5 | Cl |
| 6·97 | OEt | 5·3 | OMe | OMe | 8·8 | 3·3 | OAc |

| (XXII) (Ref. 31, 32) | | | (XXIII) (Ref. 12, 32) | | | (XXIV) (Ref. 12, 32) | | | (XXV) (Ref. 32) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $J_{AC}$ | $J_{BC}$ | X | $J_{AC}$ | $J_{BC}$ | X | $J_{AC}$ | $J_{BC}$ | X | $J_{AC}$ | $J_{BC}$ | X |
| 9·73[c] | 3·81 | H | 4·43 | 3·08 | H | 11·21 | 8·01 | H | 9·2 | 3·8 | H |
| 9·3 | 4·6 | CN | 4·2 | 2·5 | CN | 12·6 | 9·6 | SiMe₃ | 8·7 | 3·8 | COOH |
| 8·0 | 3·2 | Cl | 2·7 | 1·4 | Cl | 9·4 | 6·6 | Br | 7·4 | 2·4 | Cl |
| 7·7 | 2·5 | OAc | 2·2 | 1·4 | OAc | 8·0 | 5·4 | OAc | 7·2 | 2·5 | OAc |

[a] Only a few representative values from each of the systems are given.
[b] Average coupling constant.
[c] $J_{endo,endo}$ = 9·16 Hz.

The orientation of the substituents with respect to the fragment H–C–C–H is important, as well as their nature. This can be deduced from the fact that the lines of best fit corresponding to equation (2) constructed for various systems (*e.g.*, those in Table 1) exhibit variations in slope not only between different

[77] R. J. Abraham and K. G. R. Pachler, *Mol. Phys.*, 1964, **7**, 165.
[78] J. R. Cavanaugh and B. P. Dailey, *J. Chem. Phys.*, 1961, **34**, 1099.
[79] P. Laszlo and P. R. Schleyer, *J. Amer. Chem. Soc.*, 1963, **85**, 2709.

systems but also between $J_{cis}$ and $J_{trans}$ in the same system. Further, specific examples, the first of which (XLVI and XLVII) was reported by Bhacca and Williams[80] indicate that an electronegative substituent exerts its maximum effect (leading to the smallest $J_{vic}$) where an antiperiplanar relation exists between a part of the 'coupling path' [indicated by heavy lines in (XLVI) and (XLVII)] and the bond by which it is attached to the system, *i.e.*, as in (XLVII) but not in (XLVI).
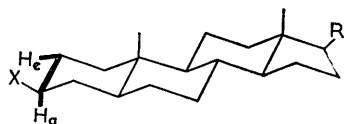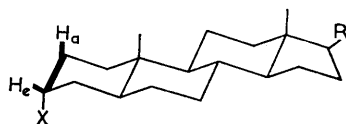


| (XLVI) | (XLVII) |
|---|---|
| X = OH, OAc | X = OH, OAc |
| $J_{ea} = 5 \cdot 5 \pm 1$ Hz | $J_{ea} = 2 \cdot 5$ to $3 \cdot 2$ Hz |

Confirmatory evidence for this relationship has been obtained by Booth[59] and others.[6,81] Further, it has been suggested that in acyclic systems[81] of known conformation, and hence presumably in the chair forms of six-membered carbocyclic rings, $J_{trans}$ in ethanic fragments is significantly affected by the presence of electronegative groups but the effect on $J_{gauche}$ can be neglected unless stereochemistry analogous to that in (XLVII) is present.

A further complication arises from the fact that most substituents are not axially symmetric about the bond by which they are attached to the system H–C–C–H and it appears that the rotation about this bond is important. This effect became apparent[5,10,60,61,76,81] in certain cyclic systems, *e.g.*, in the series of unsaturated five-membered rings (XLV),[5,61] where one would expect the vicinal coupling constants for X = O to be the *smallest*, rather than the largest, on grounds of electronegativity alone. It has therefore been suggested[10,61] that lone pairs of heteroatoms contribute a positive increment to $J_{vicinal}$ when in certain orientations with respect to the H–C–C–H system and that this increment is approximately $+2 \cdot 3$ Hz for each perfect eclipsing[10] of the lone pair on the nitrogen or oxygen with one of the carbon–hydrogen bonds. Clearly, caution must therefore be exercised in interpreting data for five-membered[6] and six-membered[82] saturated heterocyclic systems. In three-membered heterocyclic compounds the trends in coupling constants appear to follow electronegativities of the heteroatoms in a straightforward manner.[5]

The presence of an electronegative substituent at a position one carbon atom removed from the coupling path, *i.e.*, in the system X–C–CH$_A$–CH$_B$ causes an

[80] N. S. Bhacca and D. H. Williams, *J. Amer. Chem. Soc.*, 1964, **86**, 2742.
[81] R. J. Abraham, L. Cavalli, and K. G. R. Pachler, *Mol. Phys.*, 1966, **11**, 471.
[82] J. B. Lambert, *J. Amer. Chem. Soc.*, 1967, **89**, 1836; J. B. Lambert, R. G. Keske, and D. K. Weary, *J. Amer. Chem. Soc.*, 1967, **89**, 5921.

*increase* in $J_{AB}$. This phenomenon has been discovered by Cohen and Schaefer[58] and is exemplified by the values of $J_{vicinal}$ in cyclopropane[70] ($J_{cis}$ 9·5, $J_{trans}$ 5·5) and 1,1-dichlorocyclopropane[32] ($J_{cis}$ 11·21, $J_{trans}$ 8·01). Clearly, the effect is not negligible and has been noted[58,60] in other systems. There are indications that the trend reverses again[58] with the removal of the electronegative substituent one more carbon atom away from the coupling path.

**B. Vicinal Coupling in the Systems** $\overset{\|}{H-C-C-H}$ **and** $\overset{\|\ \ \|}{H-C-C-H}$**.—**Although few data[4,6,57] are available for these systems, there is little doubt that this type of vicinal coupling is closely related to that in the fully saturated systems discussed above. In acyclic systems (XLVIII) the estimated[83] values for $J_{gauche}$ and $J_{trans}$ are clearly controlled by a Karplus-type relationship and commonly encountered[4,6] average values for this fragment are 5—8 Hz. In cyclo-olefins (XLIX) the values for larger rings also appear to be controlled by the magnitudes of the dihedral angles, but the very small vicinal coupling constants in cyclo-
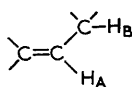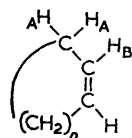


(XLVIII)

$J_{AB}$ gauche $= 1·8—3·7$
$J_{AB}$ trans $\ \ = 9·6—13·4$
(Ref. 83)



(XLIX)

| $J_{AB}$ | $n$ |
|---|---|
| 1·0 | 1 |
| 2·1 | 2 |
| 3·1 | 3 |
| 5·7 | 4 |
| 7·8 | 5 |
| 8·2 | 6 |

(Ref. 28, 84)
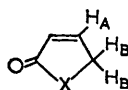


(L)

| $J_{AB}$ | X |
|---|---|
| 1·6 | O |
| 2·6 | S |

(Ref. 4)
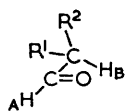


(LI)

| $J_{AB}$ | $R^1$ | $R^2$ |
|---|---|---|
| 2·85 | H | H |
| 1·17 | Me | Me |
| 6·00 | $But$ | $But$ |

(Ref. 85)
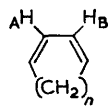


(LII)

| $J_{AB}$ | $n$ |
|---|---|
| 1·94 | 1 |
| 5·14 | 2 |

(Ref. 88, 89)

[58] A. A. Bothner-By, S. Castellano, S. J. Ebersole, and H. Gunther, *J. Amer. Chem. Soc.*, 1966, **88**, 2466, and previous papers in this series.

butene[28] and probably also cyclopentene[84] may reflect deformation in the angles H–C̈–C–H, as predicted by theory.[56] The effect of substituents in, *e.g.*, (L) is similar in direction to that found in saturated systems. Coupling of aldehydic protons to the α-protons (LI) is generally in the range of 1—3 Hz[85] and aldehyde derivatives, such as oximes, *etc.*, exhibit comparable ranges,[86] with estimated approximate values for $J_{gauche}$ 3 Hz and $J_{trans}$ 10 Hz.

$J_{H-\overset{\|}{C}-\overset{\|}{C}-H}$ in acyclic dienes and polyenes[4,87] generally take up values between 10 and 12 Hz. Cyclic systems[88,89] (LII) exhibit a range of values (2—8 Hz) presumably influenced both by angular deformations and by departures from planarity. The corresponding coupling constant in cycloheptatrienes[88] is 5·2—5·7 Hz and for cyclohexa-1,3-dienones and cyclohepta-1,3-dienones in the range[89] of 5·5—8 Hz. Finally, in derivatives of acrolein $J_{H-\overset{O}{\overset{\|}{C}}-\overset{\|}{C}H}$ is generally approximately 8 Hz.[4]
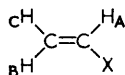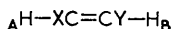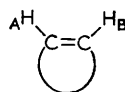
| | (LIII) | | | (LIV) | | | (LV) | |
|---|---|---|---|---|---|---|---|---|
| $J_{AB}$ | $J_{AC}$ | X | $J_{trans}$ | $J_{cis}$ | X | Y | $J_{AB}$ | Ring size |
| 23·9 | 19·3 | Li | 16·8 | 10 | H | Me | 0·5—1·5 | 3 |
| 19·1 | 11·6 | H | 15·5 | 11·4 | Me | $CO_2Me$ | 2·5—4·2 | 4 |
| 17·2 | 10·4 | $CO_2H$ | 14·4 | 11·0 | Ph | SPh | 5·1—7·0 | 5 |
| 14·3 | 7·0 | OMe | 13·1 | 7·2 | Cl | $CH_2Cl$ | 8·8—11·0 | 6 |
| 13·9 | 6·3 | OAc | 12·1 | 5·3 | Cl | Cl | 9—12·5 | 7 |
| 12·7 | 4·7 | F | 9·5 | 2·0 | F | F | 10—13 | 8 |
| | (Ref. 4, 5, 6, 36, 63, 94) | | | | | | *ca.* 11 | >8 |
| | | | | | | | (Ref. 4, 5, 6, 28, 84) | |

## C. Vicinal Coupling in the System H–X–Y–H where X and/or Y are Heteroatoms.

—Where proton exchange[2,3] is sufficiently slow (see introductory remarks above) the vicinal coupling constants $J_{H-C-O-H}$, $J_{H-C-N-H}$, and $J_{H-C-S-H}$ can be observed, and generally range from 5 to 9 Hz.[4,6] From the considerable

[84] G. V. Smith and H. Kriloff, *J. Amer. Chem. Soc.*, 1963, **85**, 2016; O. L. Chapman, *ibid.*, p. 2014; P. Laszlo and P. R. Schleyer, *ibid.*, p. 2017.
[85] G. J. Karabatsos and N. Hsi, *J. Amer. Chem. Soc.*, 1965, **87**, 2864.
[86] G. J. Karabatsos and R. A. Taller, *Tetrahedron*, 1968, **24**, 3923, and previous papers in this series.
[87] A. A. Bothner-By and R. K. Harris, *J. Amer. Chem. Soc.*, 1965, **87**, 3451; A. A. Bothner-By and D. Jung, *ibid.*, 1968, **90**, 2342; A. A. Bothner-By and D. F. Koster, *ibid.*, p. 2351 and previous papers in this series.
[88] J. B. Lambert, L. J. Durham, P. Lepoutere, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1965, **87**, 3896; H. Günther, M. Görlitz, and H. H. Hinrichs, *Tetrahedron*, 1968, **24**, 5665.
[89] A. A. Bothner-By and E. Moser, *J. Amer. Chem. Soc.*, 1968, **90**, 2347; W. Regel and W. von Philipsborn, *Helv. Chim. Acta*, 1968, **51**, 867; W. A. Bubb, and S. Sternhell, unpublished work.

amount of data for alcohols[4,6,90] it appears almost certain that $J_{H-C-O-H}$ exhibits a dependence on the dihedral angle analogous to the Karplus relation, with $J_{gauche}$ *ca.* 2 Hz and $J_{trans}$ *ca.* 12 Hz. Systematic data for $J_{H-C-N-H}$, whose values vary with electronegativity of substituents,[91] are also available.

$J_{H-C-X-H}$ and $J_{H-X-Y-H}$, where X and Y are elements of Groups IV and V occur over the range 1·5—10 Hz[6,51,53,92] and appear to exhibit some dependence on stereochemistry.

**D. Vicinal Coupling in Ethylenic Systems.**—$J(H_A-C{=}C-H_B)$ exhibits very useful and regular correlations with the nature of substituents, with the ring size in cyclic compounds and with the *cis–trans* relation between $H_A$ and $H_B$. The ranges given in the structures (LIII—LV) are representative values taken from large collections of data.[4,5,6,36,63,84,93]

The regular variation of vicinal coupling constants with substitution (*e.g.*, LIII) and the approximately additive effect of the substituents in 1,2-disubstituted ethylenes (*e.g.*, LIV) have been interpreted as a linear variation with the electronegativity of substituents,[34,35,63,93] *i.e.*, a relationship of the type shown in equation (2). In fact, as with geminal coupling constants in unsaturated systems,[36] an *inverse* relationship obtains[36] and the curve of best fit with the experimental data is of the type corresponding to equation (1). However, the magnitudes of the constants are such that, in spite of the inverse relation with electronegativity, a rule of thumb stating '$J_{vicinal}$ gets smaller as the sum of the electronegativities of substituents increases', together with consultation of tables of data[4,5,6,36,63,94] will give an unequivocal assignment of stereochemistry in 1,2-disubstituted ethylenes, even when only one isomer is present. One of the few cases (LVI) where the examination of a single isomer might[94] have led to a misassignment, owing to an unusually low $J_{trans}$:$J_{cis}$ ratio, involves unusual substituents.

Evidence exists that the effect of electronegative substituents on the vicinal coupling constants in ethylenic systems *reverses* when the substituent is removed by a further bond,[58] in analogy with fully saturated systems (see above). As this effect is not negligible (an increase of *ca.* 0·7 Hz per unit of electronegativity is indicated[58]) empirical correlations with the extensive collections of data mentioned above are indicated whenever possible. It is useful to remember that conjugation has little effect on $J_{vic}$ in alkenes.

[90] W. B. Monitz, C. F. Proanski, and T. N. Hall, *J. Amer. Chem. Soc.*, 1965, **87**, 190; C. P. Rader, *ibid.*, 1966, **88**, 1713; J. J. Uebel and H. W. Goodwin, *J. Org. Chem.*, 1966, **31**, 2040; L. K. Patterson and R. M. Hammaker, *J. Phys. Chem.*, 1966, **70**, 3745; R. D. Stolow and A. A. Gallo, *Tetrahedron Letters*, 1968, 3331; N. L. Bauld and Y. S. Rim, *J. Org. Chem.*, 1968, **33**, 1303; E. F. Kiefer, W. Gericke, and S. T. Amimoto, *J. Amer. Chem. Soc.*, 1968, **90**, 6246.
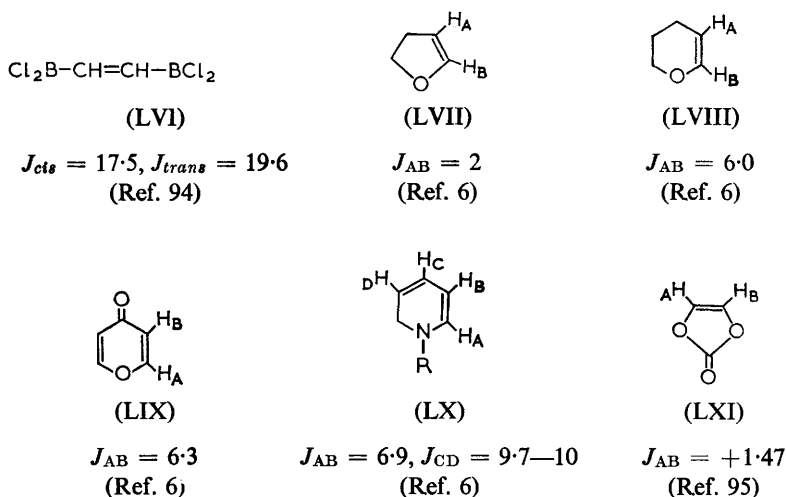
[91] I. D. Rae, *Austral. J. Chem.*, 1966, **19**, 409 and 1983.

[92] T. Birchel and W. L. Jolly, *Inorg. Chem.*, 1966, **5**, 2177.

[93] J. C. Muller, *Bull. Soc. chim. France*, 1964, 1815, 2027; J. Niwa, *Bull. Chem. Soc. Japan*, 1967, **40**, 2192.

[94] T. D. Coyle and J. J. Ritter, *J. Amer. Chem. Soc.*, 1967, **89**, 5739.

The correlation with ring sizes in cyclic systems embodied in (LV) holds not only for simple cycloalkenes, but also for non-aromatic cyclic polyenes and enones.[4,5,6,84,88,89] However, introduction of heteroatoms into the ring in a position adjacent to the double bond(s) results in a marked decrease in the (*cis*) vicinal coupling constants, in line with the relation observed in acyclic compounds. The ranges in (LV) and the examples shown in structures (LVII—LXI) are drawn from extensive collections of data[4,5,6,84] and in the case of vinylene carbonate (LXI) it can be seen that an extremely small vicinal coupling constant[95] results from a combination of a relatively small ring size and the presence of two electronegative substituents.

$$Cl_2B-CH=CH-BCl_2$$

(LVI)

$J_{cis} = 17.5, J_{trans} = 19.6$
(Ref. 94)

(LVII)

$J_{AB} = 2$
(Ref. 6)

(LVIII)

$J_{AB} = 6.0$
(Ref. 6)

(LIX)

$J_{AB} = 6.3$
(Ref. 6)

(LX)

$J_{AB} = 6.9, J_{CD} = 9.7—10$
(Ref. 6)

(LXI)

$J_{AB} = +1.47$
(Ref. 95)

It is widely believed that a lowering of the bond-order in the double bond is accompanied by a decrease in the vicinal coupling constant across it, although the dominant coupling mechanism involves only the $\sigma$ electron framework.[4,11,56] However, as the only unequivocally established examples involve bond-fixation in aromatic rings, this effect, which is believed to be due to changes in bond lengths,[56] will be discussed in the following section.

### 3 Coupling in Aromatic and Heteroaromatic Systems

From the point of view of the mechanism of spin–spin coupling, interproton coupling constants in aromatic and heteroaromatic systems do not form a well defined group. Thus it is generally implied[4,6,11,56] that the coupling between *ortho*-protons is very closely related to vicinal coupling in olefinic systems, while coupling between *meta*-protons probably[96] constitutes only a special case of long-range coupling across four single bonds in the **W** configuration.

[95] K. A. McLauchlan and T. Schaefer, *Canad. J. Chem.*, 1966, **44**, 321.
[96] M. Barfield, *J. Chem. Phys.*, 1964, **41**, 3825.

With the rare exceptions of some small coupling constants between *meta*-protons across nitrogen in six-membered rings,[97] all interproton coupling constants between aromatic protons are probably positive in sign. *ortho*-Coupling constants range from *ca.* 2 to *ca.* 9·5 Hz in six-membered and from *ca.* 1·5 to *ca.* 6 Hz in five-membered aromatic and heterocyclic rings. Coupling between *meta*-protons is generally between 0 and *ca.* 3 Hz for six-membered and between *ca.* 0·5 and *ca.* 3 Hz for five-membered aromatic and heterocyclic rings. Coupling between *para*-protons in six-membered rings is *generally* smaller than that between *meta*-protons and coupling between protons situated on different rings of polynuclear compounds is appreciable only across certain well defined paths, which will be discussed in the section dealing with long-range coupling.

While the above might indicate that the ranges of coupling constants in aromatic and heterocyclic systems are of little value in structural determination, a glance at some representative values (LXII—LXXIV) shows that, not only can one normally distinguish quite easily between *ortho, meta* and *para* coupling once the aromatic system has been identified, but that the actual values are often highly characteristic of the system. For this reason, and because the chemical shifts in aromatic compounds are very characteristic and vary regularly with substitution, the n.m.r. spectra of reasonably heavily substituted aromatic and heterocyclic compounds yield structural information very easily. Even with very lightly substituted aromatic systems the problem of interpretation of the spectra is mainly analytical.

The examples (LXII—LXXIV) were chosen from collections of data;[4,6,98] where ranges are given, they refer to rings with commonly found substituents. It can be seen that the principal effects on the magnitudes of the *ortho*-coupling
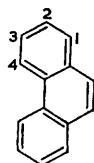


|  (LXII) |  (LXIII) |  (LXIV) |
|---|---|---|

$J_{ortho} = 6·0$—$9·5$

$J_{meta} = 1·2$—$3·3$

$J_{para} = 0·1$—$1·5$
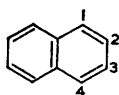
$J_{12} = 8·3$—$9·1$

$J_{23} = 6·1$—$6·9$

$J_{13} = 1·2$—$1·6$

$J_{14} = ca.\ 1$

$J_{12} = 8$ —$9$

$J_{23} = 6·9$—$7·3$

$J_{34} = 8·0$—$8·5$

$J_{13} = 0·9$—$1·6$

$J_{24} = 1·2$—$1·8$

$J_{14} = 0·3$—$0·7$

[97] R. H. Cox and A. A. Bothner-By, *J. Phys. Chem.*, 1968, **72**, 1642, 1646; J. B. Memory and J. H. Goldstein, *J. Amer. Chem. Soc.*, 1966, **88**, 5560.
[98] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution Nuclear Magnetic Resonance Spectroscopy', Pergamon Press, Oxford, 1966, volume 2, chap. 10.12—10.22; R. M. Silverstein and G. C. Bassler, 'Spectrometric Identification of Organic Compounds', Wiley, New York, 1967, 2nd edn., p. 145.

(LXV)

$J_{23} = 4\cdot0\text{---}6\cdot0$
$J_{34} = 6\cdot9\text{---}9\cdot1$
$J_{24} = 0\ \text{---}2\cdot7$
$J_{35} \sim 0\cdot5\text{---}1\cdot8$
$J_{26} \sim 0\ \text{---}0\cdot6$
$J_{25} = 0\ \text{---}2\cdot3$

(LXVI)

$J_{34} = 5\cdot1$
$J_{45} = 8\cdot0\text{---}9\cdot6$
$J_{35} = 1\cdot8$
$J_{36} = 3\cdot5$

(LXVII)

$J_{23} = 1\cdot8\text{---}3$
$J_{26} = 0 \text{ to } -0\cdot5$
$J_{25} = 1\cdot3\text{---}1\cdot8$

(LXVIII)

$J_{45} = 4\ \text{---}6$
$J_{46} = 2\cdot5$
$J_{24} = 0\ \text{---}1$
$J_{25} = 1\ \text{---}2$

(LXIX)

$J_{23} = 1\cdot3\text{---}2\cdot0$
$J_{34} = 3\cdot1\text{---}3\cdot8$
$J_{24} = 0\cdot4\text{---}1$
$J_{25} = 1\ \text{---}2$

(LXX)

$J_{23} = 4\cdot9\text{---}6\cdot2$
$J_{34} = 3\cdot4\text{---}5\cdot0$
$J_{24} = 1\cdot2\text{---}1\cdot7$
$J_{25} = 3\cdot2\text{---}3\cdot7$
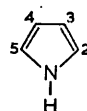
(LXXI)

$J_{12} = 1$
$J_{13} = 2$
$J_{23} = 2\cdot6$
$J_{34} = 3\cdot4$
$J_{24} = 1\cdot1$
$J_{25} = 2\cdot2$

(LXXII)

$J_{45} = \ \ 3\cdot2$
$J_{24} = \ <0\cdot5$
$J_{25} = \ \ 1\cdot9$

(LXXIII)

$J_{45} = 1\cdot6$
$J_{24} \text{ and } J_{25} = 0\cdot8\text{---}1\cdot5$
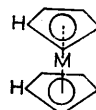
(LXXIV)

$J_{ortho} = 2\cdot3\text{---}3\cdot1$
$J_{meta} = 1\cdot0\text{---}1\cdot6$

constants are ring size and the proximity of heteroatoms and that both effects parallel closely those described above for cyclic olefins. The trends in *meta*-coupling constants are less obvious, but non-overlapping ranges are observed in some systems. Fusion of benzene rings to heteroaromatic rings has usually small effects on the coupling constants in the latter. The 'benzo' ring behaves essentially as a disubstituted benzene, except for evidence of bond-fixation (see below) in the positions predicted from drawing Kekulé forms.

Substituent effects on coupling constants in aromatic and heterocyclic systems are necessarily less pronounced for the *ortho*-coupling than for the *cis*-coupling in ethylene derivatives, as the substituent must be one carbon atom removed.

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However, systematic investigations[99,100] have uncovered regularities, the most important of which is a pronounced *increase* in $J_{2,3}$ with the increase of electronegativity of the substituent in a series of 35 monosubstituted benzenes.[100] This effect is substantial ($J_{2,3}$ 6·7 Hz in phenyl-lithium and 8·4 Hz in fluorobenzene) and affords strong support for the earlier observations of Cohen and Schaefer.[58] The second most pronounced trend, which had been noted by several authors,[6] is the tendency for *meta*-coupling constants to increase as the electronegativity of the substituent on the central carbon atom increases, *e.g.*, $J_{2,5}$ 0·74 Hz for phenyl-lithium and 2·74 for fluorobenzene.[100] It further appears that the effect of substituents on coupling constants may be additive.[99]

Considerable evidence has been accumulated[6,101] that $J_{\text{ortho}}$ is directly related to the mobile bond order across the relevant carbon–carbon bond. This is quite obvious from the inspection of the *ortho*-coupling constants in, *e.g.*, naphthalene (LXIII) and phenanthrene (LXIV), and has been utilised both as evidence for bond-fixation and for making structural assignments.[6,101] Clearly, substituent effects cited above must be taken into consideration in borderline cases or where a pronounced substituent effect is expected.

## 4 Long-range Coupling

Coupling across more than four bonds is generally designated as 'long-range coupling' although a variety of structural requirements and coupling mechanisms are involved. The maximum range of values is very large[102,103] (LXXV—LXXVI), but typically long-range coupling constants have absolute magnitudes of 0—2·5 Hz and this leads to experimental problems, associated with accurate measurement of small line separations in n.m.r. spectra.[6] Up to the present, the principal difficulty has been the poor accuracy of routinely obtained n.m.r. spectra; with most instruments, spectra recorded at sweep widths corresponding to less than 2 mm. of chart length per 1 Hz do not show line separations of less than 1 Hz. Under adverse conditions of resolution, signal:noise ratio, sweep

[99] S. Castellano and R. Kostelnik, *Tetrahedron Letters*, 1967, 5211; S. Castellano, C. Sun, and R. Kostelnik, *ibid.*, pp. 5205, 4635; S. Castellano and R. Kostelnik, *J. Amer. Chem. Soc.*, 1968, **90**, 141; J. M. Read, R. W. Crecely, R. S. Butler, J. E. Loemker, and J. H. Goldstein, *Tetrahedron Letters*, 1968, 1215; H. B. Evans, A. R. Tarpley, and J. H. Goldstein, *J. Phys. Chem.*, 1968, **72**, 2552; Y. Sasaki, M. Susuki, T. Hibino, and K. Karai, *Chem. and Pharm. Bull.*, *(Japan)* 1967, **15**, 599; T. K. Wu, *J. Phys. Chem.*, 1967, **71**, 3089; T. Schaefer, G. Kotowycz, H. M.Hutton, and J. W. S. Lee, *Canad. J Chem.*, 1968, **46**, 2531; B. Caddy, M. Martin-Smith, R. K. Norris, S. T. Reid, and S. Sternhell, *Austral. J. Chem.*, 1968, **21**, 1853.
[100] S. Castellano and C. Sun, *J. Amer. Chem. Soc.*, 1966, **88**, 4741.
[101] N. Jonathan, N. S. Gordon, and B. P. Dailey, *J. Chem. Phys.*, 1962, **36**, 2443; A. R. Katritzky and R. E. Reavill, *Rec. Trav. chim.*, 1964, **83**, 1230; A. R. Katritzky, B. Ternai, and G. J. T. Tiddy, *Tetrahedron Letters*, 1966, 1713; F. Declerck, R. Degroote, J. de Lannoy, R. Nasielski-Hinkens, and J. Nasielski, *Bull. Soc. chim. belges*, 1965, **74**, 119; J. D. Memory, G. W. Parker, and J. C. Habey, *J. Chem. Phys.*, 1966, **45**, 3567; H. Gunther, *Tetrahedron Letters*, 1967, 2967; K. D. Bartle, D. W. Jones, and J. E. Pearson, *J. Mol. Spectroscopy*, 1967, **24**, 330; W. B. Smith, W. H. Watson, and S. Chiranjeevi, *J. Amer. Chem. Soc.*, 1967, **89**, 1438; P. J. Collin, J. S. Shannon, H. Silberman, S. Sternhell, and G. Sugowdz, *Tetrahedron*, 1968, **24**, 3069; D. J. Bertelli, J. T. Gerig, and J. M. Herbelin, *J. Amer. Chem. Soc.*, 1968, **90**, 107.
[102] G. P. Newsoroff and S. Sternhell, *Tetrahedron Letters*, 1968, 6117.
[103] K. B. Wiberg, S. M. Lampmann, R. P. Ciula, D. S. Connor, P. Schertler, and J. Lavanish, *Tetrahedron*, 1965, **21**, 2749; A. Padwa, E. Shefter, and E. Alexander, *J. Amer. Chem. Soc.*, 1968, **90**, 3717.

(LXXV)

$J_{AB} = -(?)\ 3·28$ Hz

(Ref. 102)



(LXXVI)
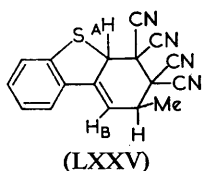
$J_{AB} = +(?)\ 18$ Hz

(Ref. 103)

speed, *etc.*, even splittings of up to 2 Hz may be missed. Poor resolution may be compensated for by the use of indirect techniques[6] or simply by taking more care but, paradoxically, the great increase of *effective* resolution already available from improved instrumentation and the use of computer analysis, and the *further* increase which must accompany improvements in decoupling techniques and the introduction of computer techniques for 'decomposition' of overlapping signals, must lead to further confusion by uncovering a great multitude of small long-range interactions. Reliable estimation of splittings as small as $0·05 ± 0·01$ Hz has in fact already been carried out in some laboratories,[104] but as this Review is concerned with the application of spin–spin coupling data to *structural* problems, we shall arbitrarily confine our attention to either well-established correlations or to coupling constants greater than *ca.* 1 Hz. The vast majority of data concerning long-range coupling is widely scattered and we shall rely on previously prepared compilations.[6,105]

Both experimental data[6,105] and theoretical and semiempirical considerations[6,11,57,63,87,96,105–112] suggest strongly that significant spin–spin interactions across more than 3 bonds are confined to certain arrangements of nuclei and bonds, *i.e.*, to 'favourable coupling paths'. In many structures more than one long-range coupling path exists and as the contributions along each may be of the same or of opposite signs, reinforcing or cancelling effects are observed.

**A. Coupling along the 'W' Path.**—Protons separated by four bonds in a planar zig-zag arrangement, usually referred to as the 'W' or 'M' configuration (LXXVII) are generally appreciably coupled independently of the nature, or hybridization, of the atoms X, Y, and Z, which may be interconnected by single or double bonds.[6,105,113] Clearly, *meta*-coupling in aromatic systems is a special

[104] R. Freeman and B. Gestblom, *J. Chem. Phys.*, 1967, **47**, 2744; R. R. Ernst, R. Freeman, B. Gestblom, and T. R. Lusebrink, *Mol. Phys.*, 1967, **13**, 283.
[105] S. Sternhell, *Rev. Pure Appl. Chem.*, 1964, **14**, 15.
[106] R. A. Hoffman, *Arkiv Kemi*, 1961, **17**, 1; R. A. Hoffman and S. Gronowitz, *ibid.*, 1961, **16**, 471, 563.
[107] M. Karplus, *J. Chem. Phys.*, 1960, **33**, 1842.
[108] E. I. Snyder and J. D. Roberts, *J. Amer. Chem. Soc.*, 1962, **84**, 1582.
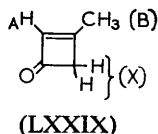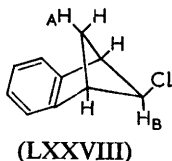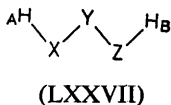[109] C. N. Banwell and N. Sheppard, *Discuss. Faraday Soc.*, 1962, **34**, 115.
[110] M. Barfield, *J. Chem. Phys.*, 1968, **48**, 4463.
[111] W. H. De Jeu, R. Deen, and J. Smidt, *Rec. Trav. chim.*, 1967, **86**, 33.
[112] H. Frischleder and G. Bar, *Mol. Phys.*, 1966, **11**, 359; A. V. Cunliffe, and R. K. Harris, *ibid.*, 1967, **13**, 269.
[113] E. W. Garbisch, *Chem. and Ind.*, 1964, 1715.

(LXXVII)  (LXXVIII)  (LXXIX)

X, Y, Z = $sp^3$ carbon, $sp^2$ carbon  $J_{AB} = +7 \cdot 4$ Hz  $J_{BX} = 1 \cdot 25$, $J_{AB} = 1 \cdot 48$,

(LXXVII fragment structure), O, N,  (Ref. 114)  $J_{AX} = 0 \cdot 63$ Hz

C , C , C and S  (Ref. 119)

$J_{AB}$ (common range) = +1 to
+3 Hz
(Ref. 6, 96, 104, 113)

case of the fragment (LXXVII). The interaction is believed to be dominated by the $\sigma$ framework[6,96,109,113] and the magnitudes of the coupling constants fall off rapidly as the system (LXXVII) loses coplanarity. Small (less than 0·5 Hz) interactions of negative sign have been observed for some non-coplanar geometries in saturated systems.[6,105] Most of the sign determinations refer to unsaturated systems,[6] but it is now known[6,114,115] that the 'W' coupling is positive also in completely saturated systems. The large values found in bicyclo[2,1,1]hexanes,[6,115] (*e.g.*, LXXVIII) presumably reflect the presence of a 'double path', but an 'indirect coupling mechanism' has also been invoked.[6,96,103] The extraordinarily large (and almost certainly positive) values in bicyclo[1,1,1]pentanes (LXXVI)[103] clearly represent a continuation of this trend. Values of the corresponding coupling constants in cyclobutanes and various bicyclic systems[6,105,116] are generally larger than those between two equatorial protons in cyclohexanes separated by four bonds and have characteristic ranges dependent on stereochemistry.

Even where the stereochemistry for long-range interaction is not very favourable, it is possible to obtain useful information from the *relative* magnitudes of the long-range coupling constants across four single bonds. Thus it is possible[6,117] to distinguish an axial tertiary methyl group (*e.g.*, the angular methyl groups at the ring junctions of steroids and terpenes), where a 'W' path to some axial

[114] K. Tori, M. Ohtsuru, Y. Hata, and H. Tanida, *Chem. Comm.*, 1968, 1096.
[115] R. J. Abraham, H. Gottschalk, H. Paulsen, and W. A. Thomas, *J. Chem. Soc.*, 1965, 6268; L. D. Hall and J. F. Manville, *Carbohydrate Research*, 1968, **8**, 295.
[116] J. W. Hanifin and G. O. Morton, *Tetrahedron Letters*, 1967, 2307; V. F. Bystrov and A. V. Stepanyats, *J. Mol. Spectroscopy*, 1966, **21**, 241.
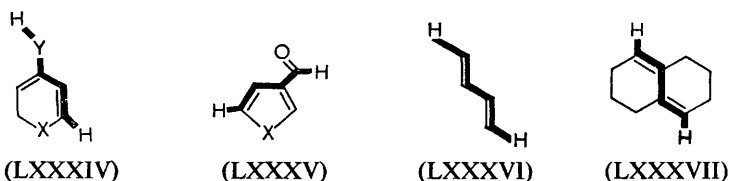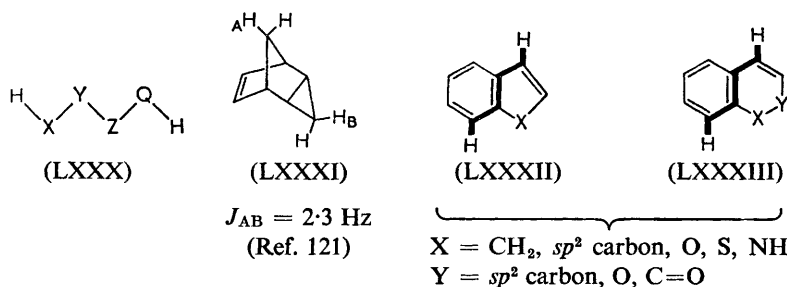[117] K. L. Williamson, T. Howell, and T. A. Spencer, *J. Amer. Chem. Soc.*, 1966, **88**, 325; C. W. Shoppee, F. P. Johnson, R. E. Lack, J. S. Shannon, and S. Sternhell, *Tetrahedron*, 1966, *Suppl.* 8, part II, 421 and references therein; R. G. Carlson and N. S. Behn, *J. Org. Chem.*, 1967, **32**, 1363; K. M. Baker and B. R. Davis, *Tetrahedron*, 1968, **24**, 1663; F. W. Bretbeil, D. T. Dennerlein, A. E. Fiebig, and R. E. Kuznicki, *J. Org. Chem.*, 1968, **33**, 3389.

ring protons is available, from an equatorial tertiary methyl group which gives rise to a narrower signal.

Similarly, geminal tertiary methyl groups are often appreciably coupled[118] and even when no splitting is discernible, it should be possible to identify such fragments by spin decoupling.

An exception to the general rule that $J_{AB}$ in (LXXVII) falls off rapidly with loss of coplanarity is the case where X and Z are $sp^3$-hybridized carbon atoms and Y is an $sp^2$ hybridized carbon atom, where $J_{AB}$ may be quite large for configurations with X, Y, and Z in one plane and both $H_A$ and $H_B$ perpendicular.[6,63,105,111,118] The largest reported value of this 'isopropylidenic'[111] coupling constant occurs in 3-methylcyclobutenone (LXXIX)[119] and the mechanism of coupling along this path is believed to involve $\sigma$–$\pi$ overlap.[6,105,111]

**B. Couplings across Five Bonds in an Extended 'Zig-Zag' Configuration and Other Interactions in Conjugated Systems**—A favourable coupling path appears to be associated with protons separated by five bonds in a planar zig-zag arrangement (*i.e.*, LXXX), and appreciable (*ca.* 0·6—1 Hz) interactions of this nature have been observed between 1,4-diequatorial protons in 1,3-dioxan and pyranose derivatives[6,120] while a much larger interaction is found in (LXXXI).[121]



(LXXX)          (LXXXI)          (LXXXII)          (LXXXIII)

$J_{AB} = 2·3$ Hz
(Ref. 121)

X = CH₂, $sp^2$ carbon, O, S, NH
Y = $sp^2$ carbon, O, C=O

(LXXXIV)          (LXXXV)          (LXXXVI)          (LXXXVII)

X = C, N          X = O, S, NH
Y = C=C, C=O, O, N

[118] C. Pascual and W. Simon, *Helv. Chim. Acta*, 1967, **50**, 94; W. J. Mijs, *Rec. Trav. chim.* 1967, **86**, 221.
[119] P. Dowd and K. Sachder, *J. Amer. Chem. Soc.*, 1967, **89**, 715; the details of the n.m.r. spectra were determined in our laboratories.
[120] J. Feeney, M. Anteunis, and G. Swalen, *Bull. Soc. chim. belges*, 1968, **77**, 121; N. S. Bhacca, D. Horton, and H. Paulsen, *J. Org. Chem.*, 1968, **33**, 2484; J. Delmau and J. Duplan, *Tetrahedron Letters*, 1966, 559
[121] K. Tori and M. Ohtsuru, *Chem. Comm.*, 1966, 886.

The planar zig-zag path is more common in unsaturated structures, where the magnitudes of the coupling constants across it are generally $+0.5$ to $+1$ Hz. The role of the $\pi$-electrons in the transmission of the effect is not entirely clear[6,87,105.109,110,112,122] but the very general occurrence of these easily detectible and stereospecific interactions along the paths indicated by heavy lines in (LXXXII)—(LXXXVII) is of diagnostic significance.[6,105] With departures from planarity, this type of interaction diminishes.

Some of the more recently discovered[123] and less usual examples are shown in structures (LXXXVIII)—(XCI) and careful observation reveals a number of smaller long-range interactions along other paths in polynuclear systems.[6,123]



(LXXXVIII)          (LXXXIX)



(XC)                    (XCI)
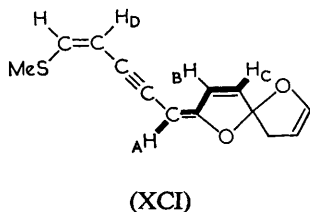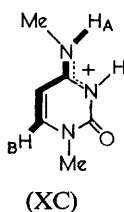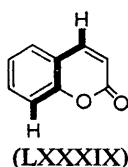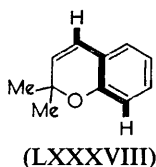
$J_{AB} = 0.7$ Hz          $J_{AB} = 0.6, J_{AC} = 1.9, J_{AD} = 2.9$ Hz

In planar conjugated systems, other appreciable (0·5—1 Hz) long-range interactions are generally also observed (*e.g.*, $J_{AB}$ in XCI), but in butadiene derivatives (LXXXVI)[6,87] the situation is complicated by conformational factors. In *cyclic* dienes, polyenes, and dienones[6,88,89] interactions along the 'W' path, with $J$ 0·4 to 3 Hz, depending upon planarity, are usually observed, and coupling across five bonds (formally similar to *para*-coupling in benzene derivatives) may be of comparable magnitude.[6,88,89]
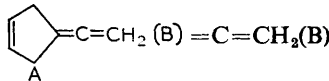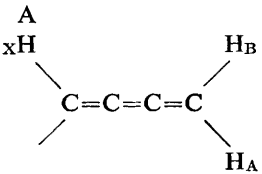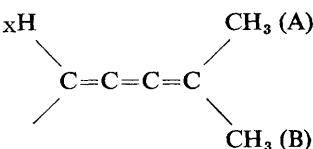
**C. Long-range Coupling in Acetylenes, Allenes and Cumulenes.**—In contrast with the above types of long-range interactions, there is little doubt that long-range coupling in these series of compounds involves the transmission of 'spin information' *via* the $\pi$-electron system and the effect can be discussed in terms of hyperconjugation.[6,105–110]

[122] G. P. Newsoroff and S. Sternhell, *Austral. J. Chem.*, 1968, **21**, 747, and references therein.
[123] E. V. Lassak and J. T. Pinhey, *J. Chem. Soc.* (*C*), 1967, 200; E. D. Becker, H. T. Miles, and R. B. Bradley, *J. Amer. Chem. Soc.*, 1965, **87**, 5575; M. W. Jarvis and A. G. Moritz, *Austral. J. Chem.*, 1968, **21**, 2445; S. Forsen and R. A. Hoffman, *J. Mol. Spectroscopy*, 1966, **20**, 168; F. Bohlmann and H. Kapteyn, *Chem. Ber.*, 1967, **100**, 1927 and previous papers in this series.

Representative values quoted in Table 2 are taken from a previous compilation,[6] except for the data for cumulenes (entries 11 and 12) for which additional results have been included.[124] Certain general features associated with transmission of long-range coupling along $\pi$-electron systems become apparent from Table 2:

**Table 2** *Long-range coupling constants in acetylenes and cumulenes*

| Entry | Structure | $J$ (Hz) |
|---|---|---|
| 1 | $H_3C-C\equiv C-H$ | 2·93 |
| 2 | $X-CH_2-C\equiv C-H$, X=Cl, Br, I | 2·6—2·8 |
| 3 | $H_3C-C\equiv C-CH_3$ | 2·7 |
| 4 | $H-C\equiv C-C\equiv C-H$ | 2·2 |
| 5 | $H_3C-C\equiv C-C\equiv C-H$ | 1·27 |
| 6 | $H_3C-C\equiv C-C\equiv C-CH_3$ | 1·3 |
| 7 | $H_3C-C\equiv C-C\equiv C-C\equiv C-CH_2-OH$ | 0·4 $[J(CH_3,CH_2)]$ |
| 8 | $R-CH=C=CH-R$ | $-5·8$ to $-6·3$ |
| 9 | $(CH_3)_2C=C=CH_2$ | 3·03 |

| 10 |  =C=CH₂ (B) =C=CH₂(B) | 4·58 $(J_{AB})$ |



| 11 | | $J_{AX} \neq J_{BX} \sim 1 - 9$ (?) |



| 12 | | $J_{AX} \neq J_{BX} \sim 1$ |

(i) The magnitude of the coupling constants attenuates relatively slowly with the number of bonds traversed, thus leading to detectable coupling across 9 bonds (entry 7).

(ii) The substitution of a methyl group for a proton at the end of the conjugated system (*cf.*, *e.g.*, the pairs of entries 1 and 3 or 5 and 6) has comparatively little effect on the *absolute* magnitude of the coupling constants although, as will be shown below, the sign of the interaction reverses. This 'methyl replacement

[124] M. Bertrand and C. Rouvier, *Compt. rend.*, 1966, **263**, 330; R. Vestin, A. Borg, and T. Lindblom, *Acta Chem. Scand.*, 1968, **22**, 685, 687; S. G. Frankiss and I. Matsubara, *J. Phys. Chem.*, 1966, **70**, 1543; P. P. Montijn, J. H. van Boom, L. Brandsma, and J. F. Arens, *Rec. Trav. chim.*, 1967, **86**, 115.

technique'[6],[106] is, in fact, considered diagnostic for the operation of the so-called 'π-coupling'.

(iii) The angular relations between allylic protons and the plane of the double bond influence the magnitude of the coupling constant. For the series of compounds shown in Table 2, this effect can be observed only for the pair of entries 9 and 10, but it will be shown to be general and very important from the structural point of view.

(iv) Although this is not evident from this collection of data, the sign of the coupling constant is positive for an interaction across an odd number of bonds and negative across an even number of bonds.

All the above features have been predicted theoretically[107],[110] and have been amply documented.
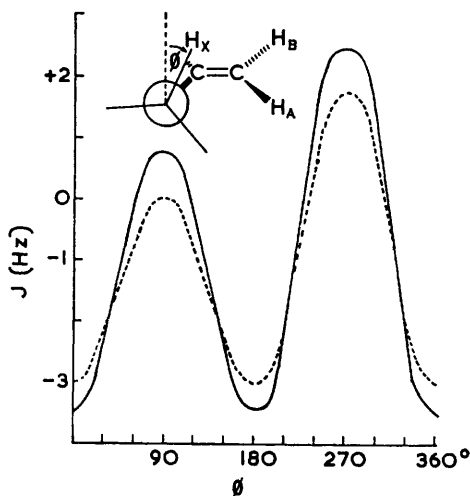


**Figure 3** *Variation of allylic coupling constants with stereochemistry.*

$- - - - J_{AX}$ (cisoid)
————— $J_{BX}$ (transoid)

**D. Allylic Coupling.**—This is the most commonly observed of all long-range interactions and can be defined as $J_{\text{allylic,cisoid}}$ ($J_{AX}$) and $J_{\text{allylic, transoid}}$ ($J_{BX}$) (Figure 3). The factors influencing the magnitude of allylic coupling constants can be summarized as follows:

(i) A variation with stereochemistry approximating that shown in Figure 3 is obeyed. This relationship, which cannot yet be considered definitive, is partially based on a very large number of data collected in our laboratories[6],[39],[102],[105] and partially on theoretical[96] and empirical[57] considerations of the combined effect of coupling *via* the 'π'[106],[110] and 'σ' paths.

(ii) Figure 3 also shows that for *large negative* values[102] and probably also for

most positive values, $|J_{transoid}| > |J_{cisoid}|$. This 'crossing' of the two curves makes the application of the very commonly observed relation for acyclic derivatives (where for negative values of *ca.* 0·7 to 1·8 Hz $|J_{cisoid}|$ is usually larger than $|J_{transoid}|$) of very doubtful value for structural determinations.[6,102]

(iii) Theory predicts[6,106,110] and experimental data confirm[6,104] that the absolute magnitude of (negative) allylic coupling constants should decrease with the decrease of the mobile bond order of the double bond. The examples (XCII), (XCIII),[125] and (XCIV)[126] complement previous data.[6,105,127] Thus allylic coupling
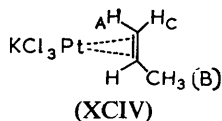


(XCII)                  (XCIII)                  (XCIV)
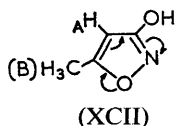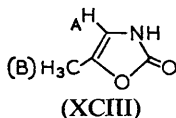
$J_{AB} = -(?)\ 0·9$ Hz     $J_{AB} = -(?)\ 1·5$ Hz     $J_{AB} \sim J_{CB} \sim 0·1$ Hz
(Ref. 125)               (Ref. 125)               (Ref. 126)

under stereochemically defined conditions [*e.g.*, for $J(H_3C-C=C-H)$] can be used as a probe[127] of bond-order, although an accurate linear relation cannot be implied[128] (see also section on benzylic coupling below).

(iv) The effect of substituents which do not affect the bond order of the double bond are not very pronounced, but are by no means negligible as can be seen from the accurate data for halogenopropenes obtained by DeWolf and Baldeschwieler.[129] However, for the purposes of determining structures, such effects can *usually* be neglected.

(v) Allylic coupling between ring protons in cyclobutenes[28,102,119] is often much smaller (*e.g.*, in LXXIX) than expected from the angular relationships in Figure 3, although the coupling between an allylic methyl group and the ring proton is normal (LXXIX). In fact $J(H_3C-C=C-H)$ appears to lie within a fairly narrow range (1·2—1·7 Hz, presumably negative sign) for all ring sizes incorporating the double bond concerned, provided that the bond order is not abnormal.

The above-mentioned 'crossing' effect[102] throws some doubt on the general applicability of the theoretical treatment.[96] Further, there is a paucity of accurate experimental data for the region of $\phi$ between *ca.* 80 and 100°, but absolute magnitudes of between 0 and 1 Hz are indicated for both $J_{transoid}$ and $J_{cisoid}$[6,96,102,113] There are also almost no data for $J_{cisoid}$ for the region of $\phi$ between *ca.* 190 and 350°, as structures embodying this configuration are rare.

In spite of the above limitations, the magnitudes of allylic coupling constants can be of great value in determining structures of organic compounds, because,

[125] H. Göth, A. R. Gagneux, C. H. Eugster, and H. Schmid, *Helv. Chim. Acta,* 1967, **50**, 137.
[126] H. P. Fritz, K. E. Schwarzhans, and D. Sellmann, *J. Organometallic Chem.*, 1966, **6**, 551.
[127] H. Rottendorf and S. Sternhell, *Austral. J. Chem.*, 1964, **17**, 1315.
[128] D. J. Blears, S. S. Danyluk, and T. Schaefer, *Canad. J. Chem.*, 1968, **46**, 654.
[129] M. Y. De Wolf and J. D. Baldeschwieler, *J. Mol. Spectroscopy*, 1964, **13**, 344.

in exact analogy with the application of the Karplus relation, the choice of stereo-chemical options nearly always involves a prediction of 'small' or 'large' allylic coupling constants (Figure 3). The not uncommon[6,130] negligible values (due to cancellation of positive and negative contributions) for transoid allylic coupling when $\phi = ca.$ 230 or 310° are also highly characteristic.

Examples of allylic coupling constants of the usual range of magnitudes[6,33,105,131] occur in systems where one of the two $sp^2$-hybridized carbon atoms has been replaced by nitrogen, *i.e.*, in fragments H–C–N=C–H. There is little doubt that coupling across the peptide bond, *i.e.*, in the fragment
$$H-\overset{\|}{\underset{\|}{C}}-\overset{\|}{\underset{|}{N}}-\overset{\|}{\underset{|}{C}}-H$$
is related to its double-bond character.[6,105,131] Allylic coupling to aldehydic protons, *i.e.*, $J_{H-\overset{O}{\overset{\|}{C}}-C-C-H}$, is generally not observable.[6,105] This is probably due to the average conformation rather than to the $sp^2$-hybridization of the carbonyl carbon atom, as analogous coupling across four bonds in butadiene derivatives[87–89] varies with stereochemistry.

**E. Homoallylic Coupling.**—This is closely related to allylic coupling, and may defined (XCV) as $J_{\text{homoallylic, cisoid}} = J_{AX}$ and $J_{\text{homoallylic, transoid}} = J_{BX}$. The factors influencing the magnitude of homoallylic coupling constants are analogous to those enumerated above for allylic coupling, but *two* angles ($\phi$ and $\phi'$) can be varied. Although the amount of data[6,104,131,132] is considerably smaller than for allylic coupling, useful regularities can be detected.

(i) Theory predicts[107,110] that the '$\pi$' coupling along the homoallylic path should be positive with $J = ca.$ 5 $\cos^2\phi \cdot \cos^2\phi'$ and a periodicity of 180°; no experimental data contradict this basic relation. Generally, $J_{H-C=C-CH_3}$ is of
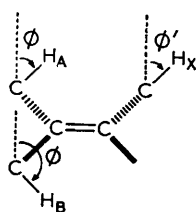


(XCV)  (XCVI)  (XCVII)

X = CH, N      X = O, NH
$J_{AB} = (+?)\ 5\cdot5$ to $(+?)\ 11$ Hz
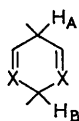
$J_{AB} = 0\cdot4$ to 7 Hz

[130] C. W. Jefford, S. N. Mahajan, and K. C. Ramey, *Chem. Comm.*, 1965, 616; C. W. Jefford, S. N. Mahajan, and J. Gunsher, *Tetrahedron*, 1968, **24**, 2921; T. Tezuka, Y. Akasaki, and T. Mukai, *Tetrahedron Letters*, 1967, 1397; H. Tanida, K. Tori, and K. Kitahonoki, *J. Amer. Chem. Soc.*, 1967, **89**, 3212.
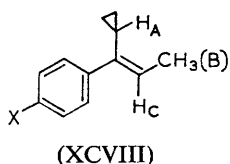[131] N. Colebourne, R. G. Foster, and E. Robson, *J. Chem. Soc. (C)*, 1967, 685; G. J. Karabatsos and S. S. Lande, *Tetrahedron*, 1968, **24**, 3907; K. Tori, M. Ohtsuru and T. Kubota, *Bull. Chem. Soc. Japan*, 1966, **39**, 1089.
[132] C. M. Cimarusti and J. Wolinsky, *J. Org. Chem.*, 1966, **31**, 4118.

approximately equal magnitude and of opposite sign to $J_{Me-C\equiv C-Me}$ (*cf.* 'methyl replacement test'[6,106]).
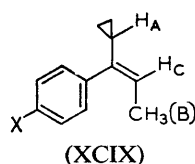
The largest homoallylic coupling constants have been observed in systems (XCVI) where the angular relations are favourable and a double homoallylic path can be postulated.[6,133] The largest homoallylic coupling over a single path so far recorded is *ca.* 5 Hz, values of up to 3 Hz being quite common.[6] Very variable and stereochemically sensitive coupling can also be observed in the system (XCVII)[6,134] where a dual path is possible.

(ii) In systems with equivalent values of $\phi$ and $\phi'$, *e.g.*, 1,2-disubstituted butenes $H_3C-CX=CY-CH_3$[6,135] transoid coupling is consistently larger (by *ca.* 0·3 Hz) than cisoid coupling, the common range of magnitudes being between $+0·8$ and $+1·7$ Hz. This has been rationalised[136] by the presence of an additional coupling path in the transoid case, namely that involving the extended five-bond zig-zag (see Section 2). The only reversals so far recorded are the isomeric systems[137] (XCVIII—XCIX), and (C—CI).[102,39] The explanation of these apparent anomalies lies almost certainly in the fact that, while each pair is geometrically isomeric, it is unlikely to be conformationally equivalent, thus
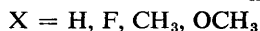


(XCVIII)

$J_{AB} = (+ ?)\ 1·1$ Hz
$J_{AC} = (- ?)\ 1·5$ Hz

(XCIX)

$J_{AB} = (+ ?)\ 0·8$ Hz
$J_{AC} = (- ?)\ 1·0$ Hz

X = H, F, CH$_3$, OCH$_3$
(Ref. 137)

(C)

$J_{AB} = (+ ?)\ 1·12$ Hz

(CI)

$J_{AB} = (+ ?)\ 1·19$ Hz

(CII)
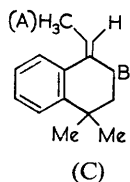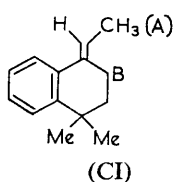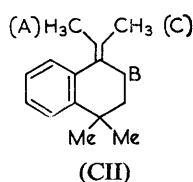
$J_{AB} = (+ ?)\ 1·4$ Hz
$J_{CB} = (+ ?)\ 1·1$ Hz

[133] M. D. Mehta, D. Miller, and E. F. Mooney, *J. Chem. Soc.*, 1965, 6695; E. W. Garbisch and M. G. Griffith, *J. Amer. Chem. Soc.*, 1968, **90**, 3590.
[134] C. Barbier, D. Gagnaire, and P. Votero, *Bull. Soc. chim. France*, 1968, 2330; K. Katagiri, K. Tori, Y. Kimura, T. Yoshida, T. Nagasaki, and H. Minato, *J. Medicinal Chem.*, 1967, **10**, 1149.
[135] H. G. Hecht and B. L. Victor, *J. Amer. Chem. Soc.*, 1967, **89**, 2532; 1968, **90**, 3333.
[136] H. Rottendorf, S. Sternhell, and J. R. Wilmshurst, *Austral. J. Chem.*, 1965, **18**, 1759.
[137] A. D. Ketley, A. J. Berlin, and L. P. Fisher, *J. Org. Chem.*, 1966, **31**, 2648.

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causing the angular ($\cos^2 \phi$) relationships, rather than the *cis–trans* geometry to become dominant. The reversed order of *allylic* coupling constants in the pair (XCVIII—XCIX) offers some confirmation for this explanation while the relative values for the homoallylic coupling constants in (CII) give a more reliable indication of the conformational nonequivalence of the pair (C—CI). The absolute magnitudes of the coupling constants in the latter set indicate the intervention of further factors, but assignments based on the relative magnitudes of cisoid and transoid homoallylic coupling constants must, *so far*, be considered unchallenged by any experimental data.

(iii) Scant experimental data[6,105,131] indicate that the relationship between homoallylic coupling constants and the bond-order of the double bond is analogous to that found for allylic coupling, and that one or more of the $sp^2$-hybridized carbon atoms can be replaced by nitrogen, or in some cases[138] even by oxygen.

**F. Benzylic Coupling.**—For the purposes of correlation of coupling constants with structure, it is convenient to define 'benzylic coupling' as the interaction between protons bonded to $sp^3$-hybridized benzylic carbon atoms and ring protons in aromatic and heteroaromatic systems. Clearly, with benzene derivatives we can distinguish interactions with aromatic protons *ortho*, *meta*, and *para* to the benzylic carbon and we shall refer to them as $J_{\text{ortho-benzylic}}$ *etc.*, with analogous subdivisions made for heteroaromatic systems. It must, however, be realized that, both from the point of view of the mechanisms of spin–spin coupling believed to be operating, and from considerations of steric requirements for effective spin–spin interactions, benzylic coupling thus defined is a rather arbitrary subdivision of the larger class of interactions between protons attached to *any* 'benzylic' atom and *any* ring proton.[6,122] We have already enumerated some interactions of this type above [*cf.*, *e.g.*, structures (LXXXIV) and (LXXXV)], and a similar relation can be postulated between $J_{2,4}$ in 1,3-butadienes[87,88] and allylic coupling.

Considerable collections of data, including some sign determinations and discussion, are available.[6,22,106,122,127,128,139] There is little doubt that *ortho-* and *para*-benzylic coupling is dominated by the '$\pi$' mechanism although the *meta*-benzylic coupling may involve more than one mechanism.[87,122]

Although the absolute magnitudes of benzylic coupling constants rarely exceed 1 Hz, from the point of view of structural correlations several useful relations can be considered fairly well established, without implying that other effects are negligible.

(i) For methyl groups, and by implication for other freely rotating alkyl groups, $J_{\text{ortho-benzylic}}$ (generally $-0.6$ to $-0.9$ Hz in benzene derivatives) is either approximately equal to, or larger than, $J_{\text{para-benzylic}}$ (generally *ca.*

[138] E. Moser and E. O. Fischer, *J. Organometallic Chem.*, 1968, **13**, 209.
[139] A. D. Cohen and K. A. McLauchlan, *Mol. Phys.*, 1965, **9**, 49; D. T. Witiak, D. B. Patel, and Y. Lin, *J. Amer. Chem. Soc.*, 1967, **89**, 1908; W. G. B. Huysmans, J. G. Westra, W. J. Mijs, H. A. Gaur, J. Vriend, and J. Smidt, *Tetrahedron Letters*, 1968, 4345.

−0·6 Hz in benzene derivatives) but *always* distinctly larger in absolute magnitude than $J_{\text{meta-benzylic}}$ which never appears to exceed +0·4 Hz.

(ii) For methyl groups, $J_{\text{ortho-benzylic}}$ is directly,[127] but not necessarily linearly,[128] related to the bond-order of the double bond involved and this coupling can be extremely useful as a semiquantitative probe for bond-fixation[6,105,127,140] in aromatic systems. This relation was very clearly shown in earlier work[106] on five-membered heteroaromatic systems.

(iii) The magnitude of $J_{\text{ortho-benzylic}}$ has an analogous (Figure 3) angular dependence on $\phi$ to $J_{\text{allylic, cisoid}}$[6,127] and has been used for stereochemical assignments.[6,141]

By analogy with allylic and homoallylic coupling, the term 'homobenzylic coupling' has been suggested[142] for the spin–spin interaction between protons bonded to adjacent benzylic carbon atoms. For methyl groups *ortho* to one another in aromatic and heterocyclic rings[6,106,139] this coupling is generally less than 0·5 Hz but in compounds where the homobenzylic protons are nearly perpendicular to the plane of the benzene ring a value of (+ ?) 1·8 Hz has been observed.[142]

**G. Miscellaneous Examples of Long-range Coupling.**—The literature abounds in examples[6,104] of long-range spin–spin interactions which do not fit in an entirely obvious manner into any of the above classifications. This probably merely reflects the artificiality of the classification system and the superficial nature of our understanding of the mechanism of spin–spin coupling in general.

Some of these interactions are quite small, but may be very useful for the purposes of structural determinations, *e.g.*, those in formates (CIII).[6,105,143] Others, *e.g.*, (CIV)—(CVII),[144–148] may be rationalised by postulating the presence of 'dual coupling paths' or of ground-state electron shifts which cause the systems to approximate to one of the above classifications. There are also several examples where methyl protons separated by as many as seven bonds[6,89,148] are appreciably coupled. The largest of these interactions [in (CVIII) and (CIX)] are *ca.* 1 Hz and, by invoking 'methyl substitution'[6,105,106]

[140] P. M. Nair and G. Gopakumar, *Tetrahedron Letters*, 1964, 708; R. F. C. Brown, I. D. Rae, and S. Sternhell, *Austral. J. Chem.*, 1965, **18**, 1211; C. L. Bell, R. S. Egan, and L. Bauer, *J. Heterocyclic Chem.*, 1965, **2**, 420; A. V. Eltsov, V. I. Minkin, and Yu. Tsereteli, *J. Org. Chem. U.S.S.R.*, 1966, **2**, 621; E. Clar, B. A. McAndrew, and M. Zander, *Tetrahedron*, 1967, **23**, 985; H. P. Fritz and C. G. Kreiter, *J. Organometallic Chem.*, 1967, **7**, 427; P. M. G. Bavin, K. D. Bartle, and D. W. Jones, *J. Heterocyclic Chem.*, 1968, **5**, 327; E. Clar, U. Sangök, and M. Zander, *Tetrahedron*, 1968, **24**, 2817.

[141] P. T. Lansbury, J. F. Bieron, and M. Klein, *J. Amer. Chem. Soc.*, 1966, **88**, 1477; A. L. Ternay and D. W. Chasar, *J. Org. Chem.*, 1968, **33**, 2237.

[142] F. P. Johnson, A. Melera, and S. Sternhell, *Austral. J. Chem.*, 1966, **19**, 1523.

[143] K. Hayamizu and O. Yamamoto, *J. Mol. Spectroscopy*, 1967, **23**, 121.

[144] W. Metlesics, T. Anton, and L. H. Sternbach, *J. Org. Chem.*, 1967, **32**, 2185; J. T. Gerig, *Tetrahedron Letters*, 1967, 4625.

[145] N. K. Hart, S. R. Johns, and J. A. Lamberton, *Austral. J. Chem.*, 1968, **21**, 1321.
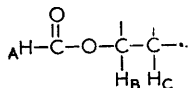
[146] A. Hoffman, W. Von Philipsborn, and C. H. Eugster, *Helv. Chim. Acta*, 1965, **48**, 1322.

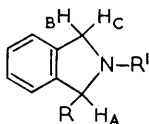[147] F. Hruska, H. M. Hutton, and T. Schaefer, *Canad. J. Chem.*, 1965, **43**, 1942.

[148] W. Steiglich and R. Hurnaus, *Tetrahedron Letters*, 1966, 384.
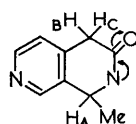
one could argue for the importance of the $\pi$-electrons in the transmission of 'spin information' along conjugated systems from these results.
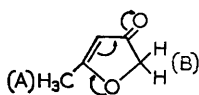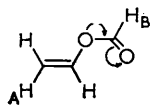


(CIII)                    (CIV)                    (CV)

$J_{AB} = -0.8$ to $-1.0$ Hz $J_{AB} \neq J_{AC} = 1$ to $3$ Hz $J_{AB}$ and $J_{AC} = 1.2$ and $1.8$ Hz
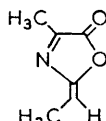$J_{AC} = +0.4$ to $+0.6$ Hz $\quad$ (Ref. 6, 144) $\qquad$ (Ref. 145)



(CVI)          (CVII)          (CVIII)          (CIX)

$J_{AB} = 0.9$ Hz $\quad$ $J_{AB} = +1.6$ Hz $\quad$ $J_{CH_3,CH_3} = ca.$ $1$ Hz
(Ref. 146) $\qquad$ (Ref. 147) $\qquad$ (Ref. 148)
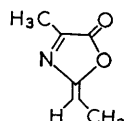
## 5 General Remarks

The Reviewer has endeavoured to delineate the usefulness of the better established correlations between the magnitudes of interproton spin–spin coupling constants and structure in an essentially empirical manner. This approach, although clearly more closely related to 'stamp collecting' than to 'physics',* is considered justified because it is obvious that the underlying cause of the boom in n.m.r. spectroscopy is its usefulness as an analytical tool in organic chemistry rather than its (very considerable) inherent interest. It is clear that at the present state of the art, the empirical approach, which amounts to argument by analogy, is less likely to lead to errors of interpretation than any attempt to apply the, necessarily simplified, theoretical treatments.

* With apologies to Lord Rutherford.