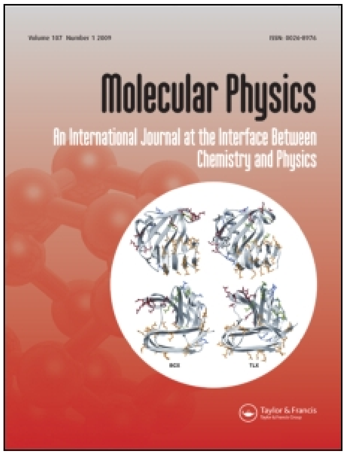

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On the spin-spin coupling between ^{13}C and H separated by two bonds

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On the spin–spin coupling between ^{13}C and H separated by two bonds

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The model of Jameson and Gutowsky which has been successful in explaining systematic trends in coupling between directly bonded nuclei is applied to coupling constants across two bonds, in particular the CCH coupling. Empirical correlations of signs and magnitudes of CCH coupling with changing bonding situations for both carbons are explained on the basis of the model and the calculated values of γ for CCH, the nature of the transfer of spin information via the electrons in the sigma bonds between the coupled nuclei (which in these calculations is expressed as a function of a collection of resonance integrals) is examined, and the applicability of the results obtained here to the XCH coupling constant is discussed. The model and the calculations are found to be successful in explaining the observed correlations in CCH couplings, and appear to hold promise of the possibility of an overall understanding of K_{XYZ} down and across the periodic table.

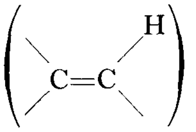
1. INTRODUCTION

Both positive and negative signs for the two-bond coupling constant $^2K_{XYZ}$ have been observed. There are scattered data (with signs) for some nuclei, and a large amount of data (only magnitudes) for many nuclei. For HCH coupling, a dependence on bond angle and electronegativity of substituents on the carbon atom has been previously noted [1]. There also appears to be a dependence of HXH on the size of X, at least in the cases (where X belongs to Group IV) in which both signs and magnitudes of the HXH coupling have been determined [2]. A look at the theory, whether by molecular orbital or valence bond treatment, reveals that $^2K_{XYZ}$ depends on a variety of exchange integrals between orbitals on X, Y and Z [1]. Since exchange integrals are very sensitive even to subtle changes in environment or angles, one would have to work out each individual case and it is not obvious that an overall understanding of two-bond coupling constants is possible. However, the above dependences which have been noticed imply that an overall understanding of $^2K_{XYZ}$ may not be out of reach.

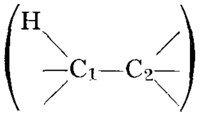
Signs of most two-bond coupling constants are not yet known, and others, especially proton–proton coupling, occur over a relatively small range of both positive and negative values. There is, however, a two-bond coupling constant, $^2K_{CCH}$, for which signs have been determined in many cases, and which have a rather wide range of magnitudes (nearly zero up to 50·8 Hz). These also afford a great variety of bonding situations in which the couplings have been measured. Furthermore, unlike other atoms, the bonding situations of carbon are fairly well defined by the number and multiplicity of the bonds. Therefore, in seeking an overall understanding of the sign and magnitude of the reduced two-bond coupling constant and its dependence on the nature of the coupled nuclei, the nature of the intervening atom, substituent and stereochemical effects, for nuclei all over the periodic table, we choose to start with the two-bond ^{13}C-proton couplings.

Inspection of C_2C_1H coupling data in the literature [3–12] leads to the following observations and correlations:

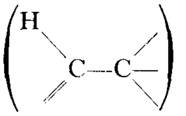
(1) *Signs and magnitudes*: ^{13}CCH coupling constants in various systems have relatively narrow spread of values within each set of bonding situations for the carbon atoms, except for the ethylenic couplings



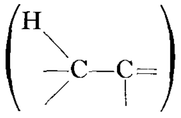
which will be considered later. These ranges are as follows:



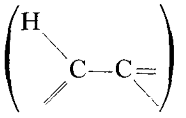
+1·2 to −5·9 Hz
(25 compounds)



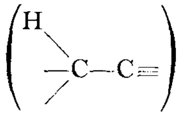
+26·6 to +46·3
(3 compounds)



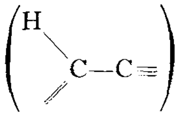
−4·0 to −7·6
(29 compounds)



(+)19·8 to (+)32·1
(8 compounds)



−8·2 to −10·6
(5 compounds)



(+)32·8
(1 compound)

(H—C≡C—) +45 to +50·8
(7 compounds)

The signs in parentheses have been assigned here as the most likely signs on the basis of comparisons with the other signs and magnitudes.

(2) *Intervening atom* (C_1) *effects*: A survey of the data in [3–12] show that, (*a*) increasing *s* character at C_1† makes $^2K_{CCH}$ more positive and larger; (*b*) electronegative substitution at C_1 likewise makes $^2K_{CCH}$ more positive. The former trend is obvious from the ranges of values above, negative for $C_1 \sim sp^3$ hybridized and increasingly positive for $C_1 \sim sp^2$ and $\sim sp$ hybridized. The latter trend is easily seen in series of related compounds like the following:

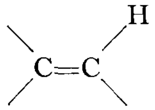
$*CH_3CH_3*$	−4·5 Hz	$*COClCH_3*$	(−)7·58	$HC{\equiv}*CCH_3*$	(−)10·6
$*CH_3CH_2*Br$	(−)2·0	$*COClCH_2*Cl$	(−)5·7	$HC{\equiv}*CCH_2*Cl$	(−)8 ·2
		$Cl*CH_2CH_2*Br$	(−)4·3	Cl_2*CHCH_3*	(−)5·1
		$Cl*CH_2CH_2*Cl$	−3·4	Cl_2*CHCH_2*Cl	(−)2·5
		$Cl*CH_2CH*Cl_2$	<2	$Cl_2*CHCH*Cl_2$	+1·2

---

† When the bonds around C_1 (and C_2) are non-equivalent, it is expected that the *s* characters of C_1 in the different bonds around C_1 (and of C_2 in the different bonds around C_2) will be different. In these cases then, the *s* characters under consideration are the *s* character of C_1 in the bonds to C_2 and H, and the *s* character of C_2 in the bond to C_1.

This is in agreement with 2 (*a*) and with the observation on other systems that electronegative substituents increase *s* character in bonds towards other atoms.

(3) *Coupled atom* (C_2) *effects*: Except for



(for which see later discussion), it appears that, (*a*) increasing *s* character at C_2† increases the absolute magnitude of K_{CCH} (we note in the ranges of values given above that negative values become more negative, positive values more positive as C_2 goes from $\sim sp^3$ to $\sim sp^2$ to $\sim sp$ hybridization). (*b*) Electronegative substitution at C_2 likewise makes $|K_{CCH}|$ greater. The latter trend is seen in series of related compounds such as:

$^*CH_3CH_3{}^*$	$-4{\cdot}5$ Hz	$^*CH_3CH^*O$	$+26{\cdot}6$	$CH_3O^*CCH_3{}^*$	$-5{\cdot}9$
$Cl_2{}^*CHCH_3{}^*$	$(-)5{\cdot}1$	$^*CHCl_2CH^*O$	$+35{\cdot}8$	$HOO^*CCH_3{}^*$	$-6{\cdot}8$
$Cl_3{}^*CCH_3{}^*$	$(-)5{\cdot}9$	$^*CCl_3CH^*O$	$+46{\cdot}3$.		

Again this is a manifestation of the above-mentioned rule on the relation between electronegative substitution and *s* character which has been found in other studies.

(4) *Effects of stereochemistry of the rest of the molecule*: The great variability in magnitude as well as in sign of the CCH coupling constants (from $-8{\cdot}5$ to nearly zero, to $+15{\cdot}4$ Hz in 15 compounds) in substituted ethylenes has been difficult to understand. It has been found by Weigert and Roberts [13] that in the multisubstituted ethylenes, the CCH coupling can be reproduced by the sum of CCH coupling constants in ethylene and the monosubstituted compounds:

$$J = J_0 + \sum_i (J_i - J_0),$$

where J_0 is the CCH coupling in ethylene, and J_i are the CCH couplings in the monosubstituted compounds. However, as was pointed out by Weigert and Roberts, there is the remaining problem of interpreting the couplings in the monosubstituted compounds themselves (see later section).

2. THEORETICAL CALCULATIONS

2.1. *The model*

In the model presented in [14] for coupling constants $^1K_{XN}$ of directly bonded nuclei, it was found that the contact contribution could be expressed as:

$$^1K_{XYZ} \simeq (1/4)\mathscr{A}_X \mathscr{A}_N / {}^3\Delta E. \tag{1}$$

Similarly, the contact contribution to two-bond coupling constants can be expressed in terms of:

$$^2K_{XYZ} \simeq (1/4)\mathscr{A}_X \gamma_{XYZ} \mathscr{A}_Z / {}^3\Delta E, \tag{2}$$

where $\mathscr{A}_X$ is the interaction corresponding to the transfer of spin information from the X nucleus to the X bonding orbital in the XY bond. γ_{XYZ} is the interaction corresponding to the transfer of electron spin information from the X bonding orbital in the XY bond to the Z bonding orbital in the YZ bond. $\mathscr{A}_Z$ is the interaction corresponding to the transfer of spin information from the Z bonding orbital in the YZ bond to the Z nucleus. $^3\Delta E$ is the mean triplet excitation energy. The interactions $\mathscr{A}_X$ and $\mathscr{A}_Z$ are the same as those cited for directly bonded nuclei, in

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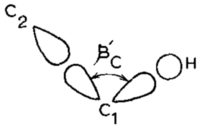
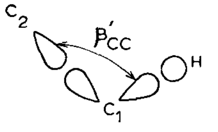
† See footnote on page 492.

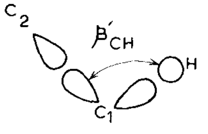
which case there is no intervening atom Y and the transfer of spin information from one electron to the other in the bond between X and Z is 100 per cent efficient since the electron spins are antiparallel in a bond. γ_{XYZ} is a function of one and two (or more) centre integrals which are sensitive to the bond angle and the nature of the substituents on the coupled nuclei and the intervening nucleus Y. It is also expected to be sensitive to the rather subtle differences in environment due to differences in stereochemistry of the rest of the molecule. The sign of γ for bond angles close to tetrahedral appears to be usually negative when there is free rotation about the bonds. For example, CCH couplings (for which $\mathscr{A}_C$ and $\mathscr{A}_H$ are both positive) [14] in ethanic systems usually have negative values. So do HCH, HSiH, SiCH, SnCH, PbCH, CdCH, and HgCH [15–17]. P(III)CH on the other hand (for which $\mathscr{A}_{P(III)}$ is negative and $\mathscr{A}_H$ is positive) [18] in systems where free rotation about all P bonds is possible, is positive. In these cases then, where free rotation is possible, the sign of γ appears to be *negative*. That is, the average value of γ over all angles of internal rotation appears to be negative, although values of γ for specific fixed stereochemical conformations may possibly have both positive and negative values, depending on the angle.

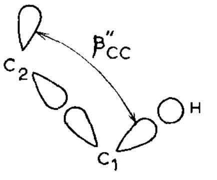
2.2. *Calculations of* γ *and* $^2K_{CCH}$

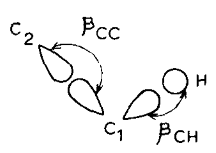
Using an independent electron molceular orbital theory by Pople and Santry [19], in principle it is possible to calculate reduced coupling constants in hydrocarbons in any configuration. For the different bonding situations in which C_2C_1H coupling constants are observed, the general method of Pople and Santry is conveniently set up in a basis set involving hybrid orbitals. The off-diagonal hamiltonian matrix elements are of two types, those between orbitals directly bonded in the primary valence structure (β_{CH} and β_{CC}) and the remainder (β_C', β_{CC}', β_{CH}' etc.) which connect orbitals in different bonds. In the calculation of coupling constants, the latter are treated as perturbations on the zeroth-order system involving only diagonal elements containing valence state ionization energies, and off-diagonal matrix elements β_{CC} and β_{CH}, each of which depend on the bonding situation. Pople and Santry applied this perturbation method in determining bonded and long-range coupling constants of ethane, ethylene and acetylene [20]. The extension of the method to the eight possible ‘ pure ’ C_2–C_1H bonding situations is straightforward. Gradations between these bonding situations are expected upon substitution of different groups at C_1 or C_2. Given below are the expressions for the off-diagonal matrix elements and $^2K_{CCH}$ for each situation. The resonance integrals involved are the following:











The mean triplet excitation energy is chosen to be -2β where β is the mean of the direct bonding interaction elements of the type β_{CC} and β_{CH}. $\mathscr{A}_{\mathrm{C}_2}$ is approximated by $(8\pi g_e\beta_e/3).\alpha_{\mathrm{C}}{}^2\phi_{\mathrm{C}}(0)^2$ where α_{C} is the coefficient of the $2s$ atomic orbital of C_2 in the bond to C_1. This does not include $1s$ core polarization contributions to $\mathscr{A}_{\mathrm{C}_2}$. $\mathscr{A}_{\mathrm{H}}$ is approximated by $(8\pi g_e\beta_e/3)\phi_{\mathrm{H}}(0)^2$. The actual $\mathscr{A}_{\mathrm{H}}$ and $\mathscr{A}_{\mathrm{C}_2}$ in the framework of the Pople–Santry molecular orbital method are somewhat different from these values, but only to the extent that the delocalized (perturbed) system is different from the completely localized zeroth-order system. Thus, in the following expressions, γ is given by $-\{\ \}/8\beta^2$.

(1) *sp*^{3}–*sp*^{3}–H

$$^2K_{\mathrm{CCH}}=(8\pi\beta_e/3)^2(1/4)\phi_{\mathrm{C}}(0)^2\phi_{\mathrm{H}}(0)^2/16\beta^3 \times\{-5\beta_{\mathrm{C}}'^2+[\beta_{\mathrm{CH}}'+\beta_{\mathrm{CC}}'+\beta_{\mathrm{CC}}''(\mathrm{trans})+2\beta_{\mathrm{CC}}''(\mathrm{gauche})]^2\}, \quad (3)$$

where

$$\beta_{\mathrm{C}}'=(1/4)(\alpha_s-\alpha_p),$$
$$\beta_{\mathrm{CH}}'=(1/2)\beta_{sh}-(1/2\sqrt{3})\beta_{\sigma h},$$
$$\beta_{\mathrm{CC}}'=(1/4)\beta_{ss}+(1/2\sqrt{3})\beta_{\sigma s}+(1/4)\beta_{\sigma\sigma},$$
$$\beta_{\mathrm{CC}}''=(1/4)\beta_{ss}-(1/2\sqrt{3})\beta_{\sigma s}-(1/12)\beta_{\sigma\sigma}+(2/3)\beta_{\pi\pi}\cos\phi,$$
$$\beta_{\mathrm{CH}}{}^{(1)}=(1/2)\beta_{sh}+(\sqrt{3}/2)\beta_{\sigma h},$$
$$\beta_{\mathrm{CC}}{}^{(1)}=(1/4)\beta_{ss}+(\sqrt{3}/2)\beta_{\sigma s}-(3/4)\beta_{\sigma\sigma},$$
$$\beta=(\beta_{\mathrm{CC}}{}^{(1)}+6\beta_{\mathrm{CH}}{}^{(1)})/7.$$

(2) *sp*^{2}–*sp*^{3} – H

$$^2K_{\mathrm{CCH}}=(8\pi\beta_e/3)^2(1/3)\phi_{\mathrm{C}}(0)^2\phi_{\mathrm{H}}(0)^2/16\beta^3 \times\{-5\beta_{\mathrm{C}}'^2+[\beta_{\mathrm{CH}}'+\beta_{\mathrm{CC}}'+\beta_{\mathrm{CC}}''(150^\circ)+\beta_{\mathrm{CC}}''(30^\circ)]^2\}, \quad (4)$$

where

$$\beta_{\mathrm{C}}'=(1/4)(\alpha_s-\alpha_p),$$
$$\beta_{\mathrm{CH}}'=(1/2)\beta_{sh}-(1/2\sqrt{3})\beta_{\sigma h},$$
$$\beta_{\mathrm{CC}}'=(1/2\sqrt{3})\beta_{ss}+(1/\sqrt{6}-1/6)\beta_{\sigma s}+(1/3\sqrt{2})\beta_{\sigma\sigma},$$
$$\beta_{\mathrm{CC}}''=(1/2\sqrt{3})\beta_{ss}-(1/6+1/2\sqrt{6})\beta_{\sigma s}-(1/6\sqrt{2})\beta_{\sigma\sigma}+(1/\sqrt{3})\beta_{\pi\pi}\cos\phi,$$
$$\beta_{\mathrm{CC}}{}^{(2)}=(1/2\sqrt{3})\beta_{ss}+(1/\sqrt{6}+1/2)\beta_{\sigma s}-(1/\sqrt{2})\beta_{\sigma\sigma},$$
$$\beta=(\beta_{\mathrm{CC}}{}^{(2)}+\beta_{\mathrm{CC}}{}^{(6)}+3\beta_{\mathrm{CH}}{}^{(1)}+\beta_{\mathrm{CH}}{}^{(6)})/6.$$

(3) *sp*–*sp*^{3}–H

$$^2K_{\mathrm{CCH}}=(8\pi\beta_e/3)^2(1/2)\phi_{\mathrm{C}}(0)^2\phi_{\mathrm{H}}(0)^2/16\beta^3 \times\{-5\beta_{\mathrm{C}}'^2+[\beta_{\mathrm{CH}}'+\beta_{\mathrm{CC}}'+\beta_{\mathrm{CC}}'']^2\}, \quad (5)$$

where

$$\beta_{\mathrm{C}}'=(1/4)(\alpha_s-\alpha_p),$$
$$\beta_{\mathrm{CH}}'=(1/2)\beta_{sh}-(1/2\sqrt{3})\beta_{\sigma h},$$
$$\beta_{\mathrm{CC}}'=(1/2\sqrt{2})\beta_{ss}+(1/2\sqrt{2}-\sqrt{3}/6\sqrt{2})\beta_{\sigma s}+(\sqrt{3}/6\sqrt{2})\beta_{\sigma\sigma},$$
$$\beta_{\mathrm{CC}}''=(1/2\sqrt{2})\beta_{ss}-(1/2\sqrt{2}+\sqrt{3}/6\sqrt{2})\beta_{\sigma s}-(\sqrt{3}/6\sqrt{2})\beta_{\sigma\sigma},$$
$$\beta_{\mathrm{CC}}{}^{(3)}=(1/2\sqrt{2})\beta_{ss}+(1/2\sqrt{2}+\sqrt{3}/2\sqrt{2})\beta_{\sigma s}-(\sqrt{3}/2\sqrt{2})\beta_{\sigma\sigma},$$
$$\beta=(\beta_{\mathrm{CC}}{}^{(3)}+\beta_{\mathrm{CC}}{}^{(8)}+3\beta_{\mathrm{CH}}{}^{(1)})/5.$$

(4) *sp*^{3}–*sp*^{2}–H

$$^2K_{\mathrm{CCH}}=(8\pi\beta_e/3)^2(1/4)\phi_{\mathrm{C}}(0)^2\phi_{\mathrm{H}}(0)^2/16\beta^3 \times\{-5\beta_{\mathrm{C}}'^2+[\beta_{\mathrm{CH}}'+\beta_{\mathrm{CC}}'+\beta_{\mathrm{CC}}''(150^\circ)+\beta_{\mathrm{CC}}''(30^\circ)+\beta_{\mathrm{CC}}''(90^\circ)]^2, \quad (6)$$

where

$$\beta_{\mathrm{C}}' = (1/3)(\alpha_s - \alpha_p),$$
$$\beta_{\mathrm{CH}}' = (1/\sqrt{3})\beta_{sh} - (1/\sqrt{6})\beta_{\sigma h},$$
$$\beta_{\mathrm{CC}}' = (1/2\sqrt{3})\beta_{ss} + (1/2 - 1/2\sqrt{6})\beta_{\sigma s} + (1/2\sqrt{2})\beta_{\sigma\sigma},$$
$$\beta_{\mathrm{CC}}'' = (1/2\sqrt{3})\beta_{ss} - (1/6 + 1/2\sqrt{6})\beta_{\sigma s} - (1/6\sqrt{2})\beta_{\sigma\sigma} + (1/\sqrt{3})\beta_{\pi\pi}\cos\phi,$$
$$\beta = (\beta_{\mathrm{CC}}{}^{(2)} + \beta_{\mathrm{CC}}{}^{(6)} + 3\beta_{\mathrm{CH}}{}^{(1)} + \beta_{\mathrm{CH}}{}^{(6)})/6.$$

(5) sp^2–sp^2–H

$${}^2K_{\mathrm{CCH}} = (8\pi\beta_{\mathrm{e}}/3)^2(1/3)\phi_{\mathrm{C}}(0)^2\phi_{\mathrm{H}}(0)^2/16\beta^3 \times \{-5\beta_{\mathrm{C}}'^2 + [\beta_{\mathrm{CH}}' + \beta_{\mathrm{CC}}' + \beta_{\mathrm{CC}}''(\mathrm{trans}) + \beta_{\mathrm{CC}}''(\mathrm{cis})]^2\}, \quad (7)$$

where

$$\beta_{\mathrm{C}}' = (1/3)(\alpha_s - \alpha_p),$$
$$\beta_{\mathrm{CH}}' = (1/\sqrt{3})\beta_{sh} - (1/\sqrt{6})\beta_{\sigma h},$$
$$\beta_{\mathrm{CC}}' = (1/3)\beta_{ss} + (1/3\sqrt{2})\beta_{\sigma s} + (1/3)\beta_{\sigma\sigma},$$
$$\beta_{\mathrm{CC}}'' = (1/3)\beta_{ss} - (\sqrt{2}/3)\beta_{\sigma s} - (1/6)\beta_{\sigma\sigma} + (1/2)\beta_{\pi\pi}\cos\phi,$$
$$\beta_{\mathrm{CC}}{}^{(5)} = (1/3)\beta_{ss} + (2\sqrt{2}/3)\beta_{\sigma s} - (2/3)\beta_{\sigma\sigma},$$
$$\beta = (\beta_{\mathrm{CC}}{}^{(5)} + 2\beta_{\mathrm{CC}}{}^{(6)} + 2\beta_{\mathrm{CH}}{}^{(6)})/5.$$

(6) $sp^2 = sp^2$–H

The same expressions as in sp^2–sp^2–H. The values for the β's are different however, since the bond lengths are different:

$$\beta_{\mathrm{CH}}{}^{(6)} = (1/\sqrt{3})\beta_{sh} + (\sqrt{2}/\sqrt{3})\beta_{\sigma h},$$
$$\beta = (\beta_{\mathrm{CC}}{}^{(6)} + 4\beta_{\mathrm{CH}}{}^{(6)})/5. \quad (8)$$

(7) sp–sp^2–H

$${}^2K_{\mathrm{CCH}} = (8\pi\beta_{\mathrm{e}}/3)^2(1/2)\phi_{\mathrm{C}}(0)^2\phi_{\mathrm{H}}(0)^2/16\beta^3 \times \{-5\beta_{\mathrm{C}}'^2 + [\beta_{\mathrm{CH}}' + \beta_{\mathrm{CC}}' + \beta_{\mathrm{CC}}'']^2\}, \quad (9)$$

where

$$\beta_{\mathrm{C}}' = (1/3)(\alpha_s - \alpha_p),$$
$$\beta_{\mathrm{CH}}' = (1/\sqrt{3})\beta_{sh} - (1/\sqrt{6})\beta_{\sigma h},$$
$$\beta_{\mathrm{CC}}' = (1/\sqrt{6})\beta_{ss} + (1/\sqrt{6} - 1/2\sqrt{3})\beta_{\sigma s} + (1/2\sqrt{3})\beta_{\sigma\sigma},$$
$$\beta_{\mathrm{CC}}'' = (1/\sqrt{6})\beta_{ss} - (1/\sqrt{6} + 1/2\sqrt{3})\beta_{\sigma s} - (1/2\sqrt{3})\beta_{\sigma\sigma},$$
$$\beta_{\mathrm{CC}}{}^{(7)} = (1/\sqrt{6})\beta_{ss} + (1/\sqrt{3} + 1/\sqrt{6})\beta_{\sigma s} - (1/\sqrt{3})\beta_{\sigma\sigma},$$
$$\beta = (\beta_{\mathrm{CC}}{}^{(7)} + \beta_{\mathrm{CC}}{}^{(8)} + \beta_{\mathrm{CC}}{}^{(6)} + \beta_{\mathrm{CH}}{}^{(6)})/4.$$

(8) $sp \equiv sp$–H

$${}^2K_{\mathrm{CCH}} = (8\pi\beta_{\mathrm{e}}/3)^2(1/2)\phi_{\mathrm{C}}(0)^2\phi_{\mathrm{H}}(0)^2/16\beta^3 . \{-5\beta_{\mathrm{C}}'^2 + [\beta_{\mathrm{CH}}' + \beta_{\mathrm{CC}}'']^2\}, \quad (10)$$

where

$$\beta_{\mathrm{C}}' = (1/2)(\alpha_s - \alpha_p),$$
$$\beta_{\mathrm{CH}}' = (1/\sqrt{2})(\beta_{sh} - \beta_{\sigma h}),$$
$$\beta_{\mathrm{CC}}'' = (1/2)(\beta_{ss} - 2\beta_{\sigma s} - \beta_{\sigma\sigma}),$$
$$\beta_{\mathrm{CC}}{}^{(8)} = (1/2)(\beta_{ss} + 2\beta_{\sigma s} - \beta_{\sigma\sigma}),$$
$$\beta_{\mathrm{CH}}{}^{(8)} = (1/\sqrt{2})(\beta_{sh} + \beta_{\sigma h}),$$
$$\beta = (\beta_{\mathrm{CC}}{}^{(8)} + 2\beta_{\mathrm{CH}}{}^{(8)})/3.$$

In evaluating the hamiltonian matrix elements the same assumptions used by Pople and Santry will be made. That is:

$$\beta_{\mu\nu}=(-10\text{ ev})S_{\mu\nu}. \tag{11}$$

Overlap integrals $S_{\mu\nu}$ were evaluated using the equations of Mulliken *et al.* [21]. The values of $\beta_{\mu\nu}$ are shown in table 1. The bond distances were taken as the average of the experimental bond distances in representative molecules. In table 2 are the values of the resonance integrals for the eight bonding stuations considered here.

C_2–C_1 bond type	R_{CC} (Å)	β_{ss}	$\beta_{\sigma s}$	$\beta_{\sigma\sigma}$	$\beta_{\pi\pi}$
(1) sp^3–sp^3	1·54	0·300	0·365	−0·328	0·192
(2) sp^2–sp^3 (4) sp^3–sp^2	1·507	0·3559	0·377	−0·3313	0·2038
(3) sp–sp^3	1·462	0·377	0·3927	−0·3326	0·2203
(5) sp^2–sp^2	1·466	0·3751	0·3913	−0·3326	0·2188
(6) $sp^2=sp^2$	1·35	0·431	0·430	−0·326	0·265
(7) sp–sp^2	1·44	0·3875	0·4002	−0·3325	0·2288
(8) $sp\equiv sp$	1·20	0·511	0·472	−0·290	0·337

Table 1. Interatomic resonance integrals, in units of −10 ev.

C_2–C_1 bond type	β_C'	β_{CH}'	β_{CC}'	β_{CC}''	β
(1) sp^3–sp^3	0·245	0·1466	0·1084	0·071 (gauche) −0·121 (trans)	0·6704
(2) sp^2–sp^3	0·245	0·1466	0·1157	$0·00199+0·1177\cos\phi$	0·6981
(3) sp–sp^3	0·245	0·1466	0·1241	−0·0178	0·7222
(4) sp^3–sp^2	0·3266	0·1466	0·0972	$0·00199+0·1177\cos\phi$	0·6981
(5) sp^2–sp^2	0·3266	0·1466	0·1064	$0·004+0·1094\cos\phi$	0·7376
(6) $sp^2=sp^2$	0·3266	0·1466	0·1363	0·1189 (cis) −0·1471 (trans)	0·7291
(7) sp–sp^2	0·3266	0·1466	0·1101	−0·0247	0·7757
(8) sp–sp	0·4900	0·0827	0·1105	−0·0715	0·7872

Table 2. Resonance integrals, in units of −10 ev.

It should be noted that in the expressions for $^2K_{CCH}$ the term $-5\beta_C'^2$ which gives a positive contribution is always present. To a first approximation this term is dependent only on the hybridization of C_1. The collection of terms in square brackets gives a negative contribution and these terms depend on the type of bonding orbitals of both C_1 and C_2. In table 3 the calculated values for γ and $^2K_{CCH}$ are given.

2.3. *Other contributions to* $^2K_{CCH}$

The pi contribution to $^2K_{CCH}$ may be calculated in terms of σ–π interaction parameters obtained from related free radicals [22]:

$$^2K_{CCH}\text{ (pi contribution)}\simeq\frac{1}{3}\sum\frac{a_Ha_C}{\Delta\pi}\cdot\frac{g_e^2\beta_e^2}{g_Cg_H\beta_N^2}\text{ cm}^{-3}, \tag{12}$$

C_1 hybridization	C_2 hybridization	Contributions to γ		γ	a_{C_2} 10^3 gauss†	$^2K_{CCH}$, 10^{20} cm^{-3}		Pi contribution 10^{20} cm^{-3}
		$5\beta_C'^2/8\beta^2$	$-[\ ]^2/8\beta^2$			Calculated	Observed	
sp^3	sp^3	+0·08348	−0·02118	+0·0623	726·2	+3·15	+0·39 to −1·9	0
	sp^2	+0·07699	−0·01820	+0·0589	968·2	+3·74	−1·3 to −2·5	+0·58
	sp	+0·07194	−0·01529	+0·0566	1452·4	+5·13	−2·7 to −3·5	+0·53
sp^2	sp^3	+0·13681	−0·01611	+0·1207	726·3	+5·75	+8·7 to +15·2	−0·20
	$(-)sp^2$	+0·12255	−0·01565	+0·1069	968·2	+6·33	(+)6·5 to 10·6	+0·78
	$(=)sp^2$	+0·12543	−0·01524	+0·1102	968·2	+6·59	See text	−0·56
	sp	+0·11079	−0·01116	+0·0996	1452·4	+8·40	(+)10·8	+0·72
sp	sp	+0·24220	−0·00296	+0·2392	1452·4	+19·89	+14·8 to +16·7	−1·66

† $\mathscr{A}_H = 288 \cdot 7 \times 10^3$ gauss. To compare with E.S.R. hyperfine splitting constants $\mathscr{A}_N$ gauss, these values have to be multiplied by $g_N\beta_N/g_e\beta_e$.

Table 3. Calculated values of γ and $^2K_{C_2C_1H}$ for various C_1 and C_2 bonding situations.

where $\Delta\pi$ is taken to be 6 ev and the sum is carried over the different σ–π pathways. The hyperfine constants a_{H} and a_{C} are given by:

$$a_{\mathrm{H}} = Q_{\mathrm{CH}}{}^{\mathrm{H}}\rho^{\pi} \quad \text{or} \quad Q_{\mathrm{CCH}}{}^{\mathrm{H}}\rho^{\pi},$$

$$a_{\mathrm{C}} = S^{\mathrm{C}} + \sum_{i=1}^{3} Q_{\mathrm{CX}_i}{}^{\mathrm{C}}\rho^{\pi} + \sum_{i=1}^{3} Q_{\mathrm{X}_i\mathrm{C}}{}^{\mathrm{C}}\rho_i{}^{\pi},$$

where $\rho^{\pi} = 1$ if there is a pi orbital on the carbon in question, otherwise $\rho^{\pi} = 0$. The sigma–pi interaction parameters Q (in gauss) are the following values calculated by Karplus and Fraenkel [23]:

$Q_{\mathrm{CH}}{}^{\mathrm{H}} = -23{\cdot}4$ for sp^2 carbon, or $-34{\cdot}7$ for sp carbon,
$Q_{\mathrm{CCH}}{}^{\mathrm{H}} = +27{\cdot}4$ when averaged over all orientations,
$S_{\mathrm{C}} = -12{\cdot}7$, $Q_{\mathrm{CC'}}{}^{\mathrm{C}} = +14{\cdot}4$, $Q_{\mathrm{C'C}}{}^{\mathrm{C}} = -13{\cdot}9$,
$Q_{\mathrm{CH}}{}^{\mathrm{C}} = +19{\cdot}2$ for sp^2 carbon, or $+38{\cdot}1$ for sp carbon.

The results are shown in the last column of table 3. The pi contributions are found to be much smaller than the observed coupling constants.

The spin–dipolar contribution to $^2K_{\mathrm{CCH}}$ in the Pople–Santry approximation is [24]:

$$^2K_{\mathrm{CCH}}(\text{spin–dipolar}) \simeq (-4/3)\beta_{\mathrm{e}}{}^2 \sum_i^{\mathrm{occ}} \sum_j^{\mathrm{unocc}} ({}^3\Delta E)^{-1} \sum_{\lambda\mu\nu\sigma} c_{i\lambda}c_{j\mu}c_{j\nu}c_{i\sigma}.$$
$$\times \sum_{\alpha,\,\beta=x,y,z} (\phi_\lambda | r_{\mathrm{C}}{}^{-5}(3r_{\mathrm{C}_\alpha}r_{\mathrm{C}_\beta} - r_{\mathrm{C}}{}^2\delta_{\alpha\beta}) | \phi_\mu)$$
$$\times (\phi_\nu | r_{\mathrm{H}}{}^{-5}(3r_{\mathrm{H}_\alpha}r_{\mathrm{H}_\beta} - r_{\mathrm{H}}{}^2\delta_{\alpha\beta}) | \phi_\sigma).$$

As was pointed out by Pople and Santry, all one-centre integrals vanish in this case where one of the nuclei is H. Non-vanishing two-centre integrals such as $(p_{\mathrm{C}} | (3z_{\mathrm{C}}{}^2 - r_{\mathrm{C}}{}^2)/r_{\mathrm{C}}{}^5 | p_{\mathrm{C}}) . (p_{\mathrm{C}} | (3z_{\mathrm{H}}{}^2 - r_{\mathrm{H}}{}^2)/r_{\mathrm{H}}{}^5 | p_{\mathrm{C}})$ are vanishingly small because in regions where $1/r_{\mathrm{C}}{}^3$ is appreciable (near the C nucleus), $1s_{\mathrm{H}}$ is small and vice versa. The orbital contribution to $^2K_{\mathrm{CCH}}$ is likewise negligible:

$$^2K_{\mathrm{CCH}}(\text{orbital}) \simeq (-16/3)\beta_{\mathrm{e}}{}^2 \sum_i^{\mathrm{occ}} \sum_j^{\mathrm{unocc}} (\Delta E)^{-1} \sum_{\lambda\mu\nu\sigma} c_{i\lambda}c_{j\mu}c_{j\nu}c_{i\sigma}$$
$$\times (\phi_\lambda | \mathbf{M}_{\mathrm{C}}/r_{\mathrm{C}}{}^3 | \phi_\mu) . (\phi_\nu | \mathbf{M}_{\mathrm{H}}/r_{\mathrm{H}}{}^3 | \phi_\sigma),$$

where $\mathbf{M}$ are orbital angular momenta which vanish for the $1s$ orbital of H. Thus, when only one-centre integrals are included the orbital contribution for $^2K_{\mathrm{CCH}}$ vanishes. Non-vanishing two-centre integrals in terms such as

$$(p_{\mathrm{C}} | \mathbf{M}_{\mathrm{C}}/r_{\mathrm{C}}{}^3 | p_{\mathrm{C}})(p_{\mathrm{C}} | \mathbf{M}_{\mathrm{H}}/r_{\mathrm{H}}{}^3 | p_{\mathrm{C}})$$

are again negligibly small. The integral on the right gives the angular momentum of the carbon $2p$ electrons about the H nucleus and is weighted by $1/r_{\mathrm{H}}{}^3$. In the regions where $1/r_{\mathrm{H}}{}^3$ is large the $2p_{\mathrm{C}}$ density is small, so the orbital contribution to $^2K_{\mathrm{CCH}}$ is likewise negligible.

3. Discussion of results and comparison with experiment

The calculated values for γ are all less than unity, as expected: the transfer of spin information being less complete than that between antiparallel electrons in a bond. From table 3 it is clear that γ becomes more positive as the intervening atom C_1 goes from sp^3 to sp^2 to sp hybridization: the positive contribution becomes larger and the negative contributions become smaller in magnitude. Pople and Santry [20] stated that the positive contribution ($5\beta_{\mathrm{C}}{}'^2$) is probably overestimated. However, this does not affect the result that γ becomes increasingly more positive as

C_1 changes hybridization from $sp^3 \rightarrow sp^2 \rightarrow sp$. We note that γ is relatively insensitive to the hybridization of the coupled atom C_2: there is but a small perceptible decrease in γ as C_2 hybridization goes from sp^3 to sp^2 to sp. On the other hand, γ is very sensitive to the hybridization of the intervening atom C_1. The changes on C_2 affect primarily $\mathscr{A}_{C_2}$ and not so much γ (the sign of γ is retained), whereas changes on C_1 affect γ to a great extent and should affect $\mathscr{A}_{C_2}$ only to a small extent (in the approximation used here changes on C_1 have no effect on $\mathscr{A}_{C_2}$ at all).

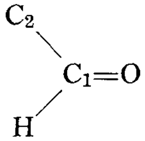
For sp^3 hybridized C_1, the positive and negative contributions are of the same order of magnitude. Since the positive contribution is overestimated, the calculation is poor and gives the wrong sign of γ and ${}^2K_{CCH}$ due to partial cancellation of the negative terms by an overestimated positive term. This is not surprising in view of Pople and Santry's results for CCH coupling in ethane in which they also had the same difficulty. The calculation of the HCH coupling is likewise beset with this difficulty, both molecular and valence bond treatments give positive couplings, in opposition to the observed negative signs [1]. Nevertheless, the calculated increase in *magnitude* of ${}^2K_{CCH}$ as C_2 goes from $\sim sp^3$ to $\sim sp^2$ to $\sim sp$ hybridization due to the increase in $\mathscr{A}_{C_2}$ agrees with experiment.

For C_1 sp^2 or sp hybridized, however, the positive terms are clearly much greater than (respectively 10-fold and 80-fold as great as) the negative terms, so that even though the positive terms are overestimated, we still expect to get the correct sign. We get a positive sign for γ, and the observed positive signs for ${}^2K_{CCH}$. The relative magnitudes of ${}^2K$ in going from sp^2 to sp hybridized C_1 are in the same order as that observed:

$$(C_1\text{–}C_2 \text{ hybridization}) \quad sp\text{–}sp > sp^2\text{–}sp > sp^2\text{–}sp^2 > sp^2\text{–}sp^3$$

even when comparing observations on systems with different kinds and number of electronegative substituents. Furthermore, regardless of sign, the calculated ${}^2K_{CCH}$ definitely increases in *magnitude* in changing C_2 hybridization from sp^3 to sp^2 to sp, since in this calculation $\mathscr{A}_{C_2}$ (and thus ${}^2K_{CCH}$) is directly proportional to $\alpha_{C_2}{}^2$. This result agrees with observed correlation (3).

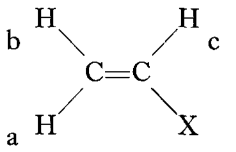
Comparison of numerical values in table 3 of ${}^2K_{CCH}$ calculated (which apply to 'pure' bonding situations such as sp^3–sp^2 etc.) and observed (which apply to gradations between these bonding situations) for sp^2 and sp hybridized C_1 show reasonable agreement of calculations with experiment. It should be noted here that most of the data compared with the theoretical $C_1 = sp^2$ are on



systems, in which the electronegative oxygen is expected to increase the s-ness of the C_1 hybrid orbitals used in bonding to the C_2 and H atoms, thus making γ more positive than that for $C_1 = sp^2$. So it is not surprising that the observed values are somewhat larger than the calculated ones, in spite of the fact that the calculated contact terms are known to be overestimated.

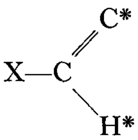
3.1. *Angular dependence of some two-bond coupling constants*

As was pointed out by Weigert and Roberts [13], although ${}^2K_{CCH}$ in the polyhaloethylenes could be explained in terms of additive CCH couplings in the monohalo-compounds, there is the remaining problem of interpreting the couplings in the monosubstituted ethylenes themselves. For the halogens, these are [13]:

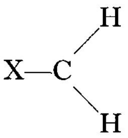


	X = Br	X = Cl	ϕ
a	−8·5	−8·3	0°
b	+7·5	+7·1	180°
c	+5·8	+6·8	

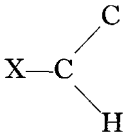
The



coupling being positive compared to that in ethylene was explained by comparing with the

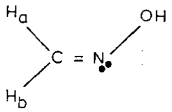
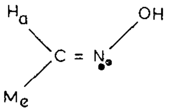
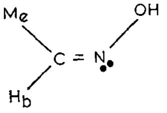
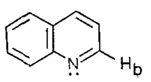


analogue, in which it has been shown that a *positive* substituent effect is associated with the electron-withdrawing effect on the CH_2 fragment by an electronegative substituent [25]. This positive substituent effect was also found by Dreeskamp and Sackmann [3] for $^2K_{CCH}$ in



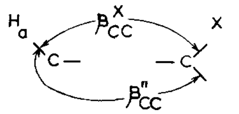
However, for CCH_a and CCH_b couplings, no explanation of the sign reversal has previously been given.

A similar angular dependence appears to be operative in NCH couplings. For example, the following NCH couplings have been reported [26]:

	$^2K_{NCH}$ (10^{20} cm^{-3})	
	a(ϕ = 0°)	b(ϕ = 180°)
	−2·2	+11·4
	−2·4	
		+13·1
		+9·0

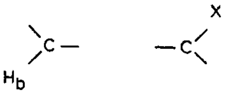
By considering the form of γ for fragments of the above molecules, as well as the monohaloethylenes, we find a possible explanation for the angular dependence:

(1)



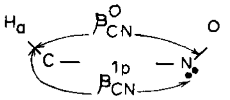
$$\gamma \simeq \{5\beta_{C}'^2 - [\beta_{CH}' + \beta_{CC}' + \beta_{CC}''(180°) + \beta_{CC}^{X}(0°)]^2\}/8\beta^2,$$

(2)



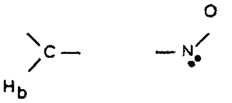
$$\gamma \simeq \{5\beta_{C}'^2 - [\beta_{CH}' + \beta_{CC}' + \beta_{CC}''(0°) + \beta_{CC}^{X}(180°)]^2\}/8\beta^2,$$

(3)



$$\gamma \simeq \{5\beta_{C}'^2 - [\beta_{CH}' + \beta_{CN}' + \beta_{CN}^{O}(0°) + \beta_{CN}^{lp}(180°)]^2\}/8\beta^2,$$

(4)



$$\gamma \simeq \{5\beta_{C}'^2 - [\beta_{CH}' + \beta_{CN}' + \beta_{CN}^{O}(180°) + \beta_{CN}^{lp}(0°)]^2\}/8\beta^2.$$

In the cases which are being compared, (1) versus (2) or (3) versus (4), the protons are coupled to the same C or N nucleus. Therefore $\mathscr{A}_C$ or $\mathscr{A}_N$ is the same. Here both $\mathscr{A}_C$ and $\mathscr{A}_N$ are positive. Thus the sign of γ determines the sign of ${}^2K_{CCH}$ or ${}^2K_{NCH}$. In all four cases, the sign of γ would be positive if the lone pair or the halogen were replaced by a hydrogen atom. If we look at case (1) versus case (2) we see that the resonance integrals in both cases are the same except for the angular dependent β_{CC}'', β_{CC}^{X}. Likewise (3) and (4) differ only by the integrals β_{CH}^{lp} and β_{CN}^{O}. We shall then examine how these resonance integrals change in going from ethylene to these specific cases.

In our calculations we had found the following: the sign of β_{CC}'' depends on the dihedral angles ϕ which are indicated in parentheses in the above equations for γ. Also, we found that the magnitude of β_{CC}'' depends on the s character of the carbon orbitals involved: this integral is large when the carbon orbitals involved in the integral are mostly p, and decreases drastically with more s participation in the orbitals in question (see table 2). When X is an electronegative atom, the carbon orbital involved in the C–X bond is such as to put more electron density close to X, that is, more carbon p orbital participation in the CX bond. Thus, β_{CC}^{X} should be large since the β'' integrals are found to increase with increasing p character. At the same time, β_{CC}'' is smaller here than when all atoms involved are either C or H, since drawing more p into the C–X bond leaves less p, more s in the other bonds of C.

Since lone pair electrons are not attracted to a second nucleus, they have high probability of being found in the region close to the N nucleus, that is, in an orbital which is s like. Therefore, β_{CN}^{lp} should be small compared to β_{CN}'' since the other N bonds, especially to the OH, will have more p character. These effects on γ are summarized below:

	(1)	(2)	(3)	(4)
$\beta_{CC}''(0°)$ or $\beta_{CN}^{lp}(0°)$		+		+ small
$\beta_{CC}^{X}(180°)$ or $\beta_{CN}^{O}(180°)$		− large		− large
$\beta_{CC}''(180°)$ or $\beta_{CN}^{lp}(180°)$	−		− small	
$\beta_{CC}^{X}(0°)$ or $\beta_{CN}^{O}(0°)$	+ large		+ large	
Effect on γ	−	+	−	+
Sign of γ	?	+	?	+
Sign of ${}^2K$, observed	−	+	−	+

Since a_N and a_C are positive, the effects on γ reflect effects on $^2K_{CCH}$ and $^2K_{NCH}$ themselves. As shown above, these qualitative arguments are in the right direction. Certainly the + signs of ^2K for the trans configurations are predicted correctly to be *enhanced positive*. Whether the negative effects are large enough remains to be determined. The Pople–Santry MO method for hydrocarbons can no longer be used here since the effects we are looking for depend on electronegativity differences which are no longer as small in these molecules as they are in C and H.

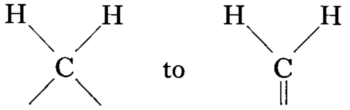
A similar angular dependence appears to be operative in P(III)CH couplings [27], although unlike the NCH and CCH couplings, the signs of the PCH couplings in those compounds of fixed stereochemistry have not yet been determined.

4. CONCLUSIONS

Except for the results for sp^3 central atom whose signs, as expected, are not in agreement with the observed values, our calculations bear out the observed correlations (2) and (3), as well as the signs observed for sp^2 and sp central atoms.

We find that, in the light of our model, the observations on $^2K_{CCH}$ are in accord with the observations on other $^2K_{XCH}$. From the observed sign of $^2K_{CCH}$ and the known + sign of $\mathscr{A}_C$ and $\mathscr{A}_H$, we deduce that the sign of γ is negative when the intervening atom is sp^3 hybridized. Since we have found that γ depends primarily on the intervening atom, in XCH where C is a saturated carbon atom, γ should likewise be negative. On the basis of our model, the sign of $^2K_{XCH}$ will depend on the sign of $\mathscr{A}_X$ ($\mathscr{A}_H$ being always positive): $^2K_{XCH}$ will be negative when $\mathscr{A}_X$ is positive, and positive when $\mathscr{A}_X$ is negative. In [14] it was found that X atoms in molecules could be classified as Case A or Case B, in which $\mathscr{A}_X$ is positive; or Case C, in which $\mathscr{A}_X$ is negative [14]. In agreement with this model, we find that in those molecules where X is a Case A or Case B nucleus, specifically H, C, Si, Sn, Pb, Cd, Hg, the $^2K_{XCH}$ values are observed to be negative [3, 15, 16]. And in those molecules where X is a Case C nucleus, specifically Se, Te and F, $^2K_{XCH}$ are observed to be positive [17]. Phosphorus is an intermediate case: Case C for P(III) and Case B for P^+(IV) and P(V) [18]. γ may well be transferable, for a given X and for a saturated carbon. Certainly the sign seems to be transferable, as we have noted above.

Our calculations show not only that γ is characteristic primarily of the central atom, but that for carbon it shows a markedly increased positive value in going from sp^3 to sp^2 to sp hybridization. This result may be more generally applicable. For example, $^2K_{HCH}$ is known to become more positive in going from



systems [28]. We also expect $^2K_{HPH}$ to become more positive in going from P(III) to P(IV) or P(V).

Note added in proof.—In view of our results, the recent values of ^{13}C–M–H couplings in transition metal compounds (WHITESIDES, G. M., and MAGLIO, G., 1969, *J. Am. chem. Soc.*, **91**, 4980) no longer appear anomalous when compared with ^{13}C–C–H couplings in organic compounds, since we have shown that the γ in two-bond couplings depend to a great extent on the nature of the intervening atom.

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