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Valence Bond Studies of Internuclear Coupling

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Two studies are reported which involve valence bond calculations of internuclear coupling. The first, of the proton spectra for the —CH_2CH_2— bridges in (2, 2) metacyclophane, shows conclusively that the relative signs of the geminal and vicinal proton coupling constants are opposite, which disagrees with the theoretical prediction that both are positive. In this compound, the C—CH_2—CH_2—C groups are locked in position with the dihedral angle between alkyl C—C—C bonds slightly less than the symmetrical, staggered 60°. A complete analysis of the A_2X_2 and A_2B_2 type proton spectra, at 60 and 15 Mc/sec leads to the following assignments: $J_t^{HH} = \pm 12{\cdot}3$, $J_{g'}^{HH}$ (the coupling of the " central " pair of gauche protons) $= \pm 3{\cdot}2$, $J_{gem}^{HH} = \mp 12{\cdot}0$, and $J_g^{HH} = \pm 4{\cdot}0$, all $\pm 0{\cdot}1$ c/sec. A second related study is concerned with an interpretation for the additivity of substituent contributions to the ^{13}C—H coupling constant. Each atom or group X is assigned a characteristic " affinity " for *s* character in the carbon hybrid orbital of the C—X bond. The additivity can be derived if the *s* character is distributed among the four carbon orbitals in accord with the relative *s* affinities of the four substituents, provided that the total *s* character is conserved. The valence bond approach used with this model gives a linear relation between the *s* character of the carbon hybrid orbital involved in a C—H bond and the observed ^{13}C—H coupling constant ($J_{CH} = 500\, \alpha_H^2$).

Valence-bond methods have been used to calculate internuclear coupling constants for non-bonded [1] and also for directly bonded nuclei.[2] For non-bonded nuclei, the σ-electron contribution to the coupling has been expressed in terms of deviations of the molecular electronic structure from perfect pairing.[1] Such calculations for protons predicted the geminal coupling J_{gem}^{HH} to be $+12{\cdot}5$ c/sec in methane,[1] and subsequent, more approximate, calculations [3] for vicinal protons in the HCCH ethanic fragment gave the trans coupling J_t^{HH} to be about $+9{\cdot}2$ c/sec and the gauche J_g^{HH}, $+1{\cdot}7$ c/sec. These magnitudes agree well with experiment except that the trans vicinal constants observed for ethanic groups [4] (and also the cis and trans constants for ethylene [3]) are often about 50 % larger than predicted. Usually, only the magnitudes of J have been obtained from experiment; but increasing attention is being given to the importance of their relative signs. Several substituted ethylenes have been reported [5, 6] in which the sign of J_{gem}^{HH} (1 to 3 c/sec) is opposite to, and also the same as, that of J_{cis}^{HH} (5 to 11 c/sec) and J_{trans}^{HH} (12 to 18 c/sec). These results are compatible with the valence-bond calculations for the CH_2 fragment,[5] which neglect substituent and π-electron effects, and which predict that J_{gem}^{HH} should become negative for HCH bond angles larger than about 120°.[5, 7] Similarly, there are substituted ethanes in which the sign of the vicinal coupling J_g^{HH} (1 to 3 c/sec) is opposite to and also the same as, that of J_t^{HH} (10 to 16·5 c/sec).[4, 6] Again, the results seem compatible with the calculated dependence of the coupling upon the dihedral angle ϕ,

$$J_{vic}^{HH} \simeq 9 \cos^2\phi - 0{\cdot}3, \tag{1}$$

because substituent effects were neglected and tetrahedral HCC angles were assumed.[3]

A more troublesome question has been raised by relative sign determinations, in diethyl sulphite [8] and in several dioxolane derivatives,[9] which conflict with the predictions [1, 3] that large values of J_{gem}^{HH} and J_{vic}^{HH} should both be positive. However, the compounds studied are such that substituent effects, angular distortions and motional averaging are important, and their neglect in the theoretical treatment might be responsible for the apparent discrepancies in the relative signs. Therefore, we have made a detailed study of the proton spectrum of the —CH_2CH_2— groups in (2, 2) metacyclophane,[10] the conformation of which is given in fig. 1. This compound avoids the uncertainties of the cases reported earlier [8, 9] because an x-ray structural determination of the solid [11] has shown that the methylene groups are locked in virtually symmetrical, staggered positions, with tetrahedral bond angles. Nonetheless, opposite signs are found for the large trans and geminal constants, in agreement with the previous experiments [8, 9] and disagreeing with the theoretical predictions that both are positive.[1, 3] This disagreement may result either from inaccurate molecular wave functions or from the approximations made in calculating the coupling of the non-bonded nuclei, and both aspects require further theoretical study.

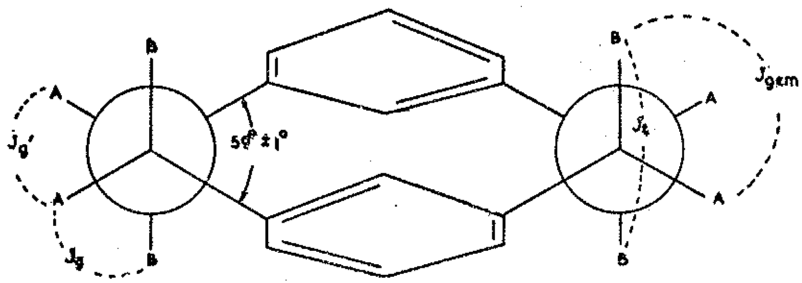

FIG. 1.—The structure of (2, 2) metacyclophane and the conformation of the —CH_2CH_2— " bridges " whose proton spectra were analyzed. The protons in the —CH_2CH_2— groups are labelled A and B, and symbols are defined for the coupling constants.

Thus far, the valence bond calculations for directly bonded nuclei appear to be more reliable. In this case, deviations from perfect pairing are relatively unimportant, and further simplification results when the coupling depends mainly on the Fermi contact term as in the ^{13}C—H group.[2] A number of theoretical and experimental studies indicate that J_{CH} is determined by the carbon orbital hybridization and by the polarity of the C—H bond.[2, 12, 13] In fact J_{CH} has been employed as a simple measure of orbital hybridization. More recently, attention has been turned to the effects of substituents upon J_{CH}, and several interesting empirical relationships have been discovered,[14, 15] the most basic of which is probably the linear additivity of group contributions to J_{CH} in substituted methanes.[14] We have found that this relation can be derived by assuming that a substituent changes the hybridization of the carbon 2*s* orbital in a characteristic fashion.[16, 17]

Substituent effects have also been noted for H—H coupling in hydrocarbons. In particular, more or less linear relations have been found between the electronegativity of the substituent and the geminal and/or vicinal coupling constants in substituted ethylenes [18-20] and ethanes.[21] As yet, no detailed, theoretical interpretation of these effects appears to have been advanced. However, it seems very probable that the effects of substituents upon J_{CH} are related directly, or at least indirectly, to those for J_{HH}. If our model is correct for the effect of X upon J_{CH} in CHXYZ or CH_2=CHX groups, it should contribute to a better understanding of J_{HH}, inasmuch as the latter is also affected by the hybridization of orbitals in the C—H bonds.

RELATIVE SIGNS OF J_{gem}^{HH}, J_g^{HH} AND J_t^{HH}

A sample of (2, 2) metacyclophane was provided for our experiments by Wilson, Boekelheide, and Griffin.[10] The high resolution proton spectra were observed at room temperature using 10% solutions in CCl_4. Spectra at 60 Mc/sec were observed with Varian Associates HR-60 and A-60 spectrometers. The 15·083 Mc/sec spectrum was obtained through the courtesy of Dr. J. N. Shoolery at Varian Associates, where it was observed with a V-4300 spectrometer system.

The general procedure used to determine the magnitudes and relative signs of the coupling constants in the $—CH_2CH_2—$ group is the following.[22] At a resonance frequency of 60 Mc/sec, the chemical shift $\nu_0\delta$ between the A_2 and B_2 sets of protons, defined in fig. 1, is sufficiently large that the quite simple observed spectrum is a good approximation to the A_2X_2 type. From it, the magnitudes of $\nu_0\delta$ and of the four coupling constants are determined readily, as well as the relative signs for each of two pairs of coupling constants. In part, the 60 Mc/sec spectrum is easy to analyze because it is insensitive to one of the relative signs. However, the latter becomes important at lower resonance frequencies, where the spectrum is of the A_2B_2 type. Therefore, the magnitudes and signs obtained from the 60 Mc/sec spectrum were used to calculate 15·083 Mc/sec spectrum for the remaining relative sign permutations, and comparison of these with the observed spectrum completes the analysis.

It is convenient to use the parameters

$$K = \pm|J_t + J_{g'}|, \qquad N = |J_g + J_{\text{gem}}|, \qquad (2)$$
$$M = |J_t - J_{g'}|, \qquad L = |J_g - J_{\text{gem}}|,$$

where the coupling constants are defined in fig. 1. These four constants have three relative signs which we wish to establish. In terms of the parameters K, L, M and N, which we treat as positive quantities except for K in the one circumstance noted below, the relative signs of each pair of coupling constants in eqn. (2) is determined by the relative values of the corresponding two parameters. Thus, if $N > L$, J_g and J_{gem} have the same sign; and if $N < L$, the opposite. Identical relations involving K and M hold for J_t and $J_{g'}$. In addition, the spectrum is sensitive to the actual relative signs of $K = (J_t + J_{g'})$ and $N = (J_g + J_{\text{gem}})$. Whether the observed spectrum is fitted by K positive or negative, while treating N as positive, determines the third relative sign. If K negative applies, then the constant of largest magnitude in K is of opposite sign to the constant of largest magnitude in N, while they are of the same sign for a positive K. Finally, the magnitudes of the coupling constants are obtained by means of eqn. (2) from the numerical (positive) values for K, L, M, and N; however, the spectrum alone does not tell which constant is which within each pair and supplemental information about the relative magnitudes of the constants is required to complete the assignment.

THE 60 Mc/sec SPECTRUM

The proton spectrum observed at 60 Mc/sec is given in fig. 2. As a first approximation it is of the A_2X_2 type, with "mirror image" A_2 and X_2 multiplets whose centres are separated by $[(\nu_0\delta)^2 + N^2]^{\frac{1}{2}}$. In general, each A_2X_2 multiplet has ten lines, two quartets and a doublet with a common centre. The outer splitting of one quartet is K, and of the other, M, while the central splittings are $(K^2+L^2)^{\frac{1}{2}} - K$ and $(M^2+L^2)^{\frac{1}{2}} - M$, respectively. The lines of the doublet are the strongest transitions; their splitting is N. In the observed spectrum, the A_2 and X_2 multiplets have two rather broad, very strong lines at the centre, with two weaker lines at each side. Therefore, the inner lines of the two quartets are not resolved from the strong N-doublet, and only the outer lines of the quartets are visible. Thus, the ~8 c/sec splitting of the strong centre pair of lines undoubtedly is N. Also, the outer splittings of the two quartets are ~9 and ~15 c/sec but at this point it is uncertain which is K and which is M. These values, in combination with the expressions for the central splitting of the two quartets and their observed values of ~8 c/sec, give an unambiguous value for L of 15 ± 2 c/sec. Also, the separation between the centres of the two multiplets is approximately the chemical shift, which gives $\nu_0\delta = 60{\cdot}3$ c/sec.

The values of the parameters were refined by varying them systematically, comparing the resulting calculated spectra [23] with experiment, and then interpolating. In this manner, the following best-fit, numerical values were obtained: $\nu_0\delta = 59{\cdot}1$, $N = 8{\cdot}0$, $L = 16{\cdot}0$, and $\pm K$ or $M = 9{\cdot}1$ or $15{\cdot}5$, all in c/sec. More important, the spectra calculated for the four possible permutations show that although the spectrum observed at 60 Mc/sec is too insensitive to the sign of K for its determination, the asymmetry in the splittings p and q in fig. 2 is governed by the relative magnitudes of K and M. In order to have $p<q$ as observed, it is necessary to have $K>M$,[22] which requires that K be 15·5 and M, 9·1 c/sec.

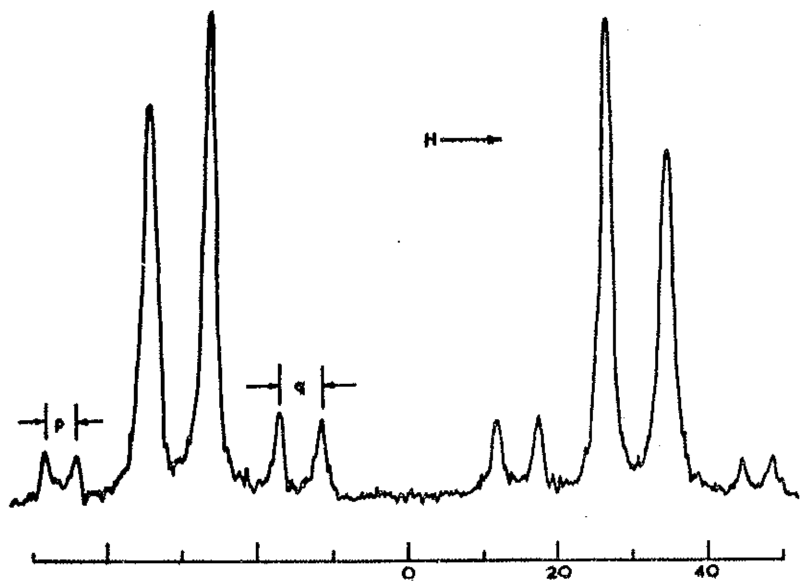

FIG. 2.—The spectrum observed at 60 Mc/sec for the —CH_2CH_2— group protons in (2, 2) metacyclophane. This spectrum is fitted by $\nu_0\delta = 59{\cdot}1$, $N = 8{\cdot}0$, $L = 16{\cdot}0$, $M = 9{\cdot}1$ and $\pm K = 15{\cdot}5$ c/sec. Spectra calculated for interchanged values of K and M have $p > q$, rather than $p < q$ as observed.

THE 15·083 Mc/sec SPECTRUM

Figure 3 includes the spectrum observed at 15·083 Mc/sec and also spectra calculated for the two remaining sign permutations, $K = \pm 15{\cdot}5$ c/sec. There is excellent agreement between experiment and the spectrum calculated for $K = -15{\cdot}5$ c/sec, and very poor agreement for $K = 15{\cdot}5$ c/sec. Therefore, the parameters which apply to the —CH_2CH_2— group are:

$$K = -15{\cdot}5 \text{ c/sec}, \quad N = 8{\cdot}0 \text{ c/sec}, \quad M = 9{\cdot}1, \quad L = 16{\cdot}0. \tag{3}$$

Upon combining these results with the definitions in eqn. (2) we find from N and L that J_g and J_{gem} are 12·0 and 4·0 or 4·0 and 12·0 c/sec. Moreover, they are of opposite signs because $N<L$. From K and M, J_t and $J_{g'}$ are 12·3 and 3·2 c/sec or the reverse. Also, they are of the same sign because $K>M$. (Here, both K and M must be treated as positive quantities.) Also K and N actually have opposite signs so the largest constant of the K, M pair (12·3 c/sec) is of opposite sign to the largest constant of the N, L pair (12·0 c/sec).

The assignment is completed by introducing the inequality $|J_t| > |J_{g'}|$, which is known with certainty from the nmr studies of substituted ethanes,[4, 6] and the inequality $|J_{gem}| > |J_g|$ which is equally certain from the experimental results [4, 6] for substituted ethanes in combination with those on J_{gem} in methane [1] and substituted methanes.[5] The final assignment is

$$J_t^{HH} = \pm 12{\cdot}3 \text{ c/sec}, \qquad J_{gem}^{HH} = \mp 12{\cdot}0 \text{ c/sec},$$
$$J_{g'}^{HH} = \pm 3{\cdot}2, \qquad J_g^{HH} = \pm 4{\cdot}0 \tag{4}$$

with probable errors of about $\pm 0{\cdot}1$ c/sec in the numerical values.

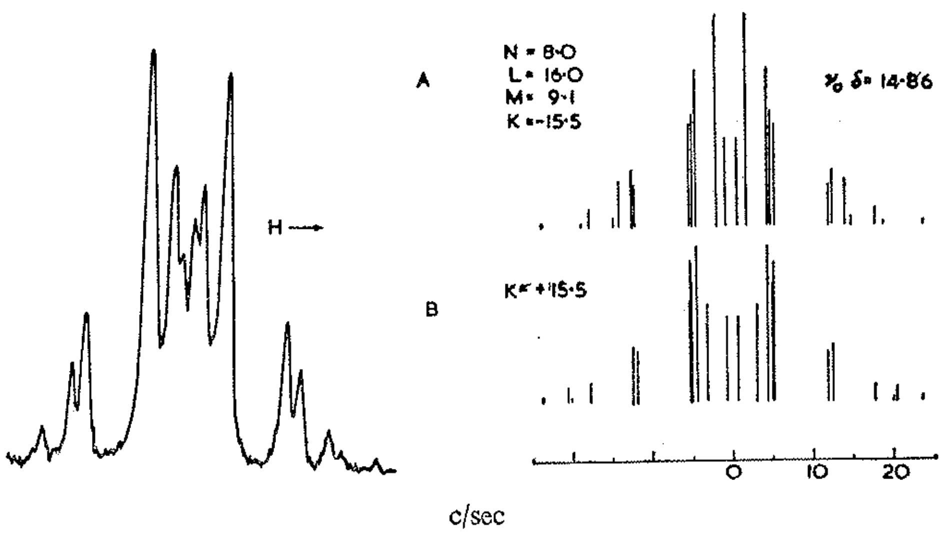

FIG. 3.—The left-hand spectrum is that observed at 15·083 Mc/sec for the —CH_2CH_2— group protons in (2, 2) metacyclophane. The line spectra at the right were calculated for the two sign permutations not differentiated by the 60 Mc/sec spectrum, i.e. for $K = \pm 15{\cdot}5$ c/sec. The spectrum for K positive disagrees with the wings and the central portion of the observed spectrum.

COMMENTS

The closeness of the $12{\cdot}0 \pm 0{\cdot}1$ c/sec value found for J_{gem}^{HH} to the $12{\cdot}4 \pm 0{\cdot}6$ c/sec observed in methane [1] indicates that the former is not affected by angular distortion and substituent effects. The small difference between the 3·2 and 4·0 c/sec values for $J_{g'}^{HH}$ and J_g^{HH} is consistent with a C—C—C—C dihedral angle of slightly less than the 60° for a symmetric, staggered —CH_2CH_2— group, as is suggested by the X-ray data for the solid.[11] Also, this could account for the value of 12·3 c/sec for J_t^{HH} being smaller than most found for substituted ethanes.[6, 7] Therefore, our finding of large values of opposite sign for J_t^{HH} and J_{gem}^{HH}, as well as the less conclusive earlier studies,[8, 9] show that either the calculation on CH_4 [1] or that on the ethanic (and probably also on the ethylenic) fragment [3] is in error. Which of the calculations is most likely to be in error, if not both, is another question. In *some* ways, the calculations for the HCCH fragment present the best opportunities for error. These calculations are more complex than for CH_4 (or CH_2), and it is possible for example that the non-neighbouring-atom exchange integrals should not have been neglected.[3] A more direct approach to the question would be to determine the sign of J_{vic}^{HH} and/or J_{gem}^{HH} with respect to J_{CH} for there is little doubt but that it is positive.[2, 17] Such relative sign determinations could help decide which of the J_{HH} calculations to redo first. Fortunately, the relative signs of J_{CH}, J_{gem}^{HH} and J_{vic}^{HH} can be determined by the sort of approach used here and also by double resonance methods, either on ^{13}C enriched (2, 2) metacyclophane or other appropriate compounds.

In fact, analysis of the ^{31}P and proton spectra observed for diphosphine H_2PPH_2 has given results,[24] related to our problem. For this compound, J^{HH}_{gem} and J_{PP} were found to have values of 108·2 and 12 c/sec, respectively, and to be of the same sign, opposite to that of J^{HH}_{vic} (cis and trans) which has values of 10·5 and 6·8 c/sec. By analogy to the results of the HCCH calculations,[3] it was assumed [24] that J^{HH}_{vic} was positive in diphosphine, which, of course, made J_{PP} and J^{HH}_{gem} negative. A negative value for J_{PP} is surprising because the coupling between directly bonded atoms due to the usually dominant contact term is positive. In view of the present findings it *may be* somewhat more plausible to take J_{PP} as positive, which leads to J^{HH}_{gem} positive and J^{HH}_{vic} (cis and trans) negative, at least in the diphosphine case.

EFFECTS OF SUBSTITUENTS UPON J_{CH}

Malinowski has reported [14] that to a very good approximation the ^{13}C—H coupling constant in substituted methanes, CHXYZ, is an additive property of the substituents. This additivity has been expressed in two equivalent forms [14, 17] employing different definitions of the " substituent parameters ". What is perhaps a better formulation may be obtained by returning to the basic experimental fact, namely,[14, 17]

$$J_{CH}(CHXYZ) = J_{CH}(CH_3X) + J_{CH}(CH_3Y) + J_{CH}(CH_3Z) - 2J_{CH}(CH_4), \tag{5}$$

and noting that it may be written as

$$J_{CH}(CHXYZ) = J_{CH}(CH_4) + \delta_X + \delta_Y + \delta_Z, \tag{6}$$

where, by definition

$$\delta_X = J_{CH}(CH_3X) - J_{CH}(CH_4). \tag{7}$$

In other words, each substituent X contributes a characteristic term δ_X, to J_{CH}(CHXYZ), which is independent of the other substituents.

There are two general approaches to the theoretical interpretation of this empirical result. Previous work [2, 12, 13] is consistent with J_{CH} being determined by the carbon orbital hybridization and the C—H bond polarity. Therefore, one can seek to derive eqn. (6) on the basis of hybridization and/or polarity changes produced in the C—H bond by the substituent. Or one can investigate the other contributions, such as π-electron and orbital polarization terms, which X could make to J_{CH} without affecting materially the C—H bond. We are concerned here with the first approach.

VALENCE BOND FORMULATION FOR J_{CH}

The general expression for $J_{NN'}$ consists of several terms.[25] However, in this paper we consider only the Fermi contact term which is dominant for the ^{13}C—H coupling, at least in CH_4,[2]

$$J_{CH} \approx (J_{CH})_{contact} = \frac{-2}{3h\Delta E}\left(\frac{16\pi\beta\hbar}{3}\right)^2 \gamma_C\gamma_H\left(\Psi_0 \,\middle|\, \sum_{k,j} \delta(\mathbf{r}_{kC})\delta(\mathbf{r}_{jH})\mathbf{S}_k\cdot\mathbf{S}_j \,\middle|\, \Psi_0\right). \tag{8}$$

The symbols used above have their usual meanings. In the ground state wave function Ψ_0 deviations from perfect pairing are not important for the coupling of directly bonded nuclei.[2] We use the separated electron pair wave function,

$$\Psi_0 = (8!)^{-\frac{1}{2}} \sum_P (-1)^P P[\Psi_{ax}(1,2)\psi_{by}(3,4)\psi_{cz}(5,6)\psi_{dh}(7,8)], \tag{9}$$

with

$$\psi_r(i,j) = u_r(i,j)\left(\frac{\alpha(i)\beta(j) - \beta(i)\alpha(j)}{\sqrt{2}}\right), \tag{10}$$

where $u_r(i,j)$ is of the valence bond form with inclusion of ionic terms,

$$u_1(1,2) = \eta_1(\phi_a(1)\phi_x(2) + \phi_a(2)\phi_x(1) + \lambda_a\phi_a(1)\phi_a(2) + \lambda_x\phi_x(1)\phi_x(2)). \tag{11}$$

In the latter, $\phi_a, \ldots \phi_d$ are carbon atomic orbitals; $\phi_x, \ldots \phi_h$ are atomic orbitals on the atoms bonded to the carbon, and η is the normalization constant. The coefficients of the ionic terms are λ_a and λ_x. Substituting Ψ_0 into eqn. (8) and using the Dirac identity $\mathbf{S}_k \cdot \mathbf{S}_j = (\frac{1}{4})(2P^s_{kj}-1)$, in which P^s_{kj} is an operator interchanging the spins of electrons k and j, one obtains

$$J_{CH} = \frac{\gamma_C\gamma_H}{h\Delta E}\left(\frac{16\pi\beta\hbar}{3}\right)^2 \eta^2(\phi_d\,|\,\delta(\mathbf{r}_{iC})\,|\,\phi_d)(\phi_h\,|\,\delta(\mathbf{r}_{jH})\,|\,\phi_h). \tag{12}$$

We assume the four carbon hybrid orbitals to be formed from one $2s$ orbital and three $2p$ orbitals, e.g.

$$\phi_d = \alpha_H s + (1-\alpha_H{}^2)^{\frac{1}{2}} p_\sigma \text{ and } \phi_a = \alpha_X s + (1-\alpha_X{}^2)^{\frac{1}{2}} p_{\sigma'}, \tag{13}$$

where the s character, α^2_H, α^2_X, etc., of the orbitals depends on the groups or atoms H, X, Y or Z bonded to the carbon. Substituting ϕ_d, and $\phi_h \equiv 1s_H$ into eqn. (12), one finds that

$$J_{CH} = \frac{\gamma_C\gamma_H}{h\Delta E}\left(\frac{16\pi\beta\hbar}{3}\right)^2 \eta^2\alpha^2_H\,|\,2s_C(0)\,|^2\,|\,1s_H(0)\,|^2, \tag{14}$$

where

$$\eta^{-2} = (2+(2+\lambda_C\lambda_H)[\alpha^2_H S^2_s + (1-\alpha^2_H)S^2_p + 2\alpha_H(1-\alpha^2_H)^{\frac{1}{2}}S_sS_p] + 4(\lambda_C+\lambda_H)\times [\alpha_H S_s + (1-\alpha^2_H)^{\frac{1}{2}}S_p] + \lambda^2_C + \lambda^2_H). \tag{15}$$

$2s_C(0)$ is the $2s$ wave function of carbon evaluated at the carbon nucleus, and $1s_H(0)$ is the corresponding quantity for the hydrogen $1s$ function. S_s and S_p are the overlap integrals between the hydrogen $1s$ atomic orbital and the $2s$ and $2p$ carbon atomic orbitals, respectively. In eqn. (15) for η^{-2}, λ_H is much less than λ_C, because the electronegativity of C is greater than that of H, so λ_H is neglected and the coefficient of the ionic contribution to the wave function is hereafter denoted by λ_{C-H}.

Eqn. (14) leads to

$$J_{CH} = (A\eta^2/\Delta E)\alpha^2_H \equiv J_0\alpha^2_H \text{ c/sec}, \tag{16}$$

where A is a collection of constants, and J_0 is 500 c/sec, as determined from the observed value [12, 13] of 125 c/sec for $J_{CH}(CH_4)$. This value for J_0 is consistent with the valence bond theory inasmuch as Karplus and Grant [2] obtained a reasonable value of 0·374 for λ_{C-H}, using the same approach, with J_{CH} = 124 c/sec, in combination with an estimate of ΔE and calculations of the overlap integrals from Hartree-Fock functions. Eqn. (16), depending upon the sensitivity of ΔE and η^2 to substituents, affords an attractive semi-empirical way to obtain the s character of bonding orbitals from coupling constants. For the substituted methanes, or other classes of closely related compounds, one would expect ΔE to be very nearly constant. This follows from the fact that it is approximately twice the bond energy,[2] which varies by only a few percent for C—H bonds. The constancy of η^2 depends upon its sensitivity to λ and α^2_H. These dependences can be calculated relatively simply and directly by means of eqn. (15). For the C—H bond, η^2 was found [17] to be insensitive to the value of α^2_H, the total change being only 0·2% over a range of α^2_H from 0·24 to 0·45. η^2 is also relatively insensitive to λ_{C-H}. Substituents are expected to change the electronegativity of the C atom by at most 0·1 to 0·2 units according to estimates of effective electronegativities by proton chemical shift measurements.[26] The empirical values of λ_{B-H}, λ_{C-H} and λ_{N-H} given by Karplus and Grant,[2] indicate that an increase in electronegativity of the carbon by 0·2 units would change λ_{C-H} from 0·374 to about 0·44. This corresponds to a decrease in η^2 to about 0·95 $\eta^2(CH_4)$.

However, the increase in λ_{C-H} is accompanied by an increase of Z_{eff} for the 2*s* and 2*p* electrons of carbon which leads to a decrease in the overlap integrals S_s, S_p, and to an increase in η^2. Thus, the effects tend to cancel, and even though α_H^2, λ_{C-H}, and the overlap integrals all change with the substituents, η^2 is expected to remain about the same for the substituted methanes. This leads to $J_0 \cong 500$ c/sec and the linear relation in eqn. (16) between J_{CH} and α_H^2.

THE ADDITIVITY OF SUBSTITUENT EFFECTS

The additivity relation observed by Malinowski [14] can be derived by means of eqn. (16) providing one assumes that the substituents redistribute the carbon 2*s* orbital among the four bonds in a particular manner. First of all, the 2*s* character must be conserved, that is

$$\alpha_H^2+\alpha_X^2+\alpha_Y^2+\alpha_Z^2 = 1. \tag{17}$$

Secondly, each atom or group X is assigned a " characteristic affinity for *s* character ", Δ_X. Let Δ_X be measured with respect to H so that Δ_X is positive if the " *s* affinity " of X is less than H and negative if greater than H. Consider the four bonds to be four equivalent interconnected potential wells of possibly different depths. The difference in the depths of the wells for X and H is defined as Δ_X. The 2*s* orbital will distribute itself among the wells to give a common 2*s* level, because of their interconnection. Moreover, this common 2*s* level, and the content of each well, can be obtained very readily via eqn. (17), i.e. by the assumption that the sum of the 2*s* content of the four wells is unity.

In CH_4 or CX_4 the four wells are all of the same depth so that 2*s* character is distributed equally among them, and $\alpha^2 = \frac{1}{4}$. In CH_3X, the H wells are deeper than that of X by the amount Δ_X which is distributed equally among four bonds so an H well will have $(\frac{1}{4})\Delta_X$ 2*s* character more than an H well in CH_4. In general, the H well in CHXYZ will have $[(\frac{1}{4})\Delta_X+(\frac{1}{4})\Delta_Y+(\frac{1}{4})\Delta_Z]$ 2*s* character more than an H well in CH_4. Expressed mathematically, this means that for CH_3X

$$\alpha_H^2(CH_3X) = \alpha_H^2(CH_4)+(\tfrac{1}{4})\Delta_X \text{ or } (\tfrac{1}{4})\Delta_X = \alpha_H^2(CH_3X)-\alpha_H^2(CH_4), \tag{18}$$

and for CHXYZ,

$$\alpha_H^2(CHXYZ) = \alpha_H^2(CH_4)+(\tfrac{1}{4})(\Delta_X+\Delta_Y+\Delta_Z). \tag{19}$$

By means of eqn. (16), α_H^2 can be eliminated from eqn. (18), giving

$$(\tfrac{1}{4})\Delta_X J_0 = J_{CH}(CH_3X)-J_{CH}(CH_4) \equiv \delta_X, \tag{20}$$

which in turn converts eqn. (19) into the observed additivity relation, eqn. (6)

$$J_{CH}(CHXYZ) = J_{CH}(CH_4)+\delta_X+\delta_Y+\delta_Z. \tag{6}$$

In addition, a general equation, similar to eqn. (19), may be written for the *s* character of the carbon orbital in the C—X bond,

$$\alpha_X^2(CHXYZ) = (\tfrac{1}{4})(1+\Delta_X+\Delta_Y+\Delta_Z)-\Delta_X. \tag{21}$$

COMPARISON WITH EXPERIMENT

Experimental values [2, 14] of $J_{CH}(CH_3X)$ and the resulting Δ_X obtained from them by means of eqn. (20) are given in table 1 for a number of substituents. The Δ_X tend to follow the electronegativity of X, being negative for electropositive substituents (−0·096 for Al) and positive for electronegative (+0·2 for the halogens). However, at least another factor is important because for substituents with the same electronegativity, Δ_X is larger for those which have the greater number of lone pair electrons.

Moreover, Δ_X is virtually the same for the four halogens in spite of their large range of electronegativity. Qualitatively, the Δ_X values are consistent with charge and spin correlation effects [17] in CH_3X, but their detailed significance remains to be determined.

TABLE 1.—SUBSTITUENT PARAMETERS Δ_X OBTAINED FROM J_{CH} OBSERVED IN SOME CH_3X COMPOUNDS

CH_3X	$J_{CH}(CH_3X)$ c/sec	α_H^2	Δ_X	CH_3X	$J_{CH}(CH_3X)$ c/sec	α_H^2	Δ_X
$Al_2(CH_3)_6$	113	0·226	−0·096	$CH_3C{\equiv}CH$	132	0·264	+0·056
$Si(CH_3)_4$	118	0·236	−0·056	CH_3NH_2	133	0·266	+0·064
CH_4	125	0·250	0·000	CH_3CCl_3	134	0·268	+0·072
CH_3CH_3	126	0·252	+0·008	CH_3CN	136	0·272	+0·088
$CH_3\phi$	126	0·252	+0·008	CH_3SH	138	0·276	+0·104
CH_3CHO	127	0·254	+0·016	$(CH_3)_2S$	138	0·276	+0·104
CH_3CH_2Br	128	0·256	+0·024	CH_3OH	141	0·282	+0·128
CH_3CH_2Cl	128	0·256	+0·024	$CH_3O\phi$	143	0·286	+0·144
CH_3COOH	130	0·260	+0·040	CH_3F	149	0·298	+0·192
CH_3CHCl_2	131	0·262	+0·048	CH_3Cl	150	0·300	+0·200
CH_3CH_2I	132	0·264	+0·056	CH_3I	151	0·302	+0·208
CH_3NHCH_3	132	0·264	+0·056	CH_3Br	152	0·304	+0·216

The effects of substituents upon α_H^2 are additive to within an accuracy of 2% for about 20 polysubstituted methanes.[14, 17] This may be seen in fig. 4 where the observed coupling constants J_{CH} are plotted against α_H^2 values predicted by means of eqn. (19) from the Δ_X values in table 1. Also plotted in fig. 4 are the J_{CH} values observed [12, 13, 27] for the 16 unsaturated hydrocarbons listed in table 2. The calculations carried out for the methanes were extended to J_{CH} in these sp^2 and sp hybridized

TABLE 2.—J_{CH} OBSERVED IN HYDROCARBONS WITH sp^2 AND sp HYBRIDIZATION, AND VALUES "PREDICTED" FOR α_H^2 IN ETHYLENES USING THE Δ_X VALUES FROM SUBSTITUTED METHANES

compound	J_{CH} c/sec	α_H^2	compound	J_{CH} c/sec	α_H^2
naphthalene	157	sp^2	$CH_2{=}CCl_2$	166	0·349
benzene	159	sp^2	$CH_2{=}^{13}CHCl$	195	0·402
mesitylene	160	sp^2	cis $CHCl{=}CHCl$	198	0·408
$(CH_3)_2C{=}C{=}^{13}CH_2$	166	sp^2	trans $CHCl{=}CHCl$	199	0·408
cyclohexene	170	sp^2	$CCl_2{=}CHCl$	201	0·416
ethylene	157	0·336	$CH_3C{\equiv}^{13}C{-}H$	248	sp
$CHCl{=}^{13}CH_2$ (cis)	160	0·341	$\phi C{\equiv}^{13}C{-}H$	251	sp
$CHCl{=}^{13}CH_2$ (trans)	161	0·341	$H{-}C{\equiv}C{-}C{\equiv}C{-}H$	259	sp

compounds. Using $\lambda_{C-H} = 0{\cdot}374$ and the overlap integrals [28] appropriate to the C—H bond distances in ethylene and acetylene, we find η^2 for these two compounds to be 0·987 η^2 (CH_4) and 0·977 η^2 (CH_4) respectively. Moreover, $\eta^2/\Delta E$ for ethylene and acetylene is affected no more by substituent effects than it is for the methanes. Hence $J_{CH} \cong 500\alpha_H^2$ for sp^2 and sp hybridized carbon, as well as for sp^3, except for possible effects of the π electrons. There does not appear to be any simple way of estimating the substituent effects upon α_H^2 for the cyclic and acetylenic compounds, so the "pure" sp^2 and sp values of $\frac{1}{3}$ and $\frac{1}{2}$ are used without correction in fig. 4. The resulting points scatter somewhat more than those for the polysubstituted methanes, but the agreement with the theoretical line is still good.

α_H^2 can be estimated for the substituted ethylenes by using the Δ_X values obtained from the methanes. The main difference is that there are three σ bonds instead of four. Also, the substituent CYZ in CYZ=CHX has no counterpart in the methanes. However, it seems reasonable to use Δ_{CHYZ} (methane) for Δ_{CYZ} (ethylene). On this basis the *s* character for a monosubstituted ethylene is given by

$$\alpha_H^2(CH_2 = {}^{13}CHX) = (\tfrac{1}{3})[1+\Delta_{CH_2}+\Delta_X] = \alpha_H^2(CH_2 = CH_2)+(\tfrac{1}{3})\Delta_X, \qquad (22)$$

which with eqn. (16) gives rise to

$$J_{CH}(CH_2 = {}^{13}CHX) = J_{CH}(CH_2 = CH_2)+(\tfrac{4}{3})[J_{CH}(CH_3X)-J_{CH}(CH_4)]. \qquad (23)$$

Values of α_H^2 predicted by means of eqn. (22) are listed for eight substituted ethylenes in table 2 and plotted, as open circles, in fig. 4 against the observed J_{CH}.

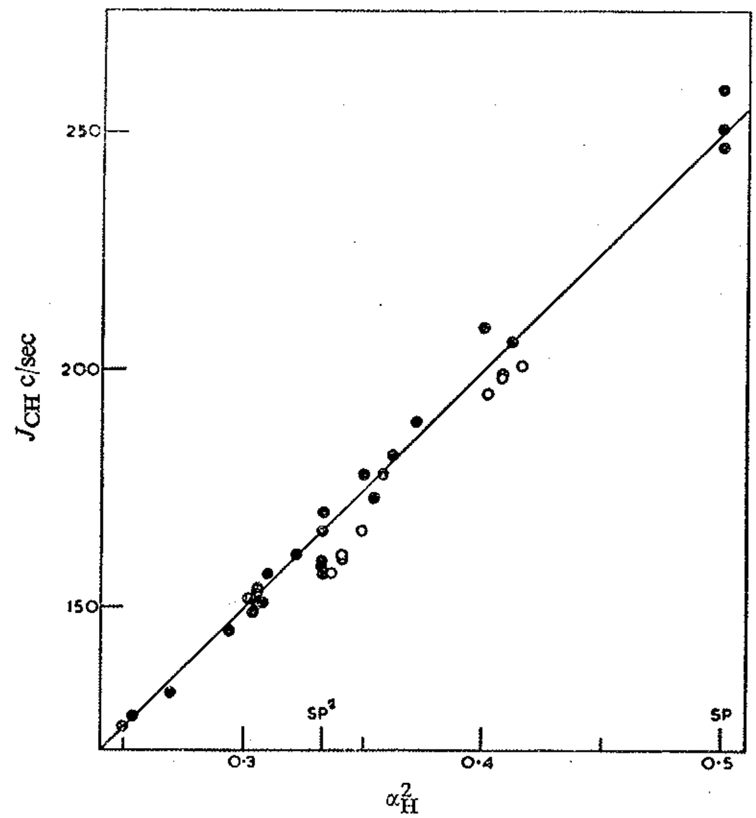

FIG. 4.—Observed J_{CH} values plotted against predicted values of α_H^2. The straight line is $J_{CH} = 500\,\alpha_H^2$ c/sec, upon which all points would fall if the methods for predicting α_H^2 were sufficiently accurate. The points for sp^2 and sp hybridization are from table 2, with no corrections for substituent effects. The open circles are for the substituted ethylenes in table 2, for which α_H^2 was predicted using the Δ_X values obtained from substituted methanes. The other points represent polysubstituted methanes for which α_H^2 was predicted by eqn. (19).

It may be seen that these data are consistently 5 to 10 c/sec below the theoretical line. It seems likely that this discrepancy may result from a π electron contribution to J_{CH}. An estimate [17] of J_{CH}^{π} for ethylene gives a value of $-2{\cdot}6$ c/sec, which is of the same sign and magnitude as the discrepancy.

A less satisfactory feature of our results is their relation to observed bond angles. The " interorbital " angles [29] corresponding to the hybridization parameters obtained from J_{CH} data are consistently smaller than the observed H—C—X and X—C—X angles. In the methyl halides, CH_3X, the calculated H—C—X angles are about 102° while those observed are 107°; and for CH_2X_2 the calculated X—C—X angles are 100° and the observed, 112°. In other words the α_H^2 values appear to be too large. These differences, at least in part, could reflect deviations from orbital following [30] of the same nature as those found in CH_2Cl_2 for which both the H—C—H and the Cl—C—Cl bond angles are greater than tetrahedral. Also, part of the substituent effect, δ_X, may result from other than a change in α_H^2. Interactions between electrons in the C—X bond and those in C—H can contribute to J_{CH}, without affecting α_H^2, and have the required additivity. The values for δ_X range from -12 to $+27$ c/sec compared to the 125 c/sec value for J_{CH} in methane itself. Even relatively small non-α_H^2 effects of about 5 c/sec would materially improve the picture. Such contributions might come from the neglected O_1 and O_2 terms [2] and/or from overlap terms [15] which were assumed to be negligible in our calculation of the Fermi contact interaction. Further studies of this question as well as of the nonadditivity of substituent effects found for J_{SiH} in silanes [16, 17] are indicated.

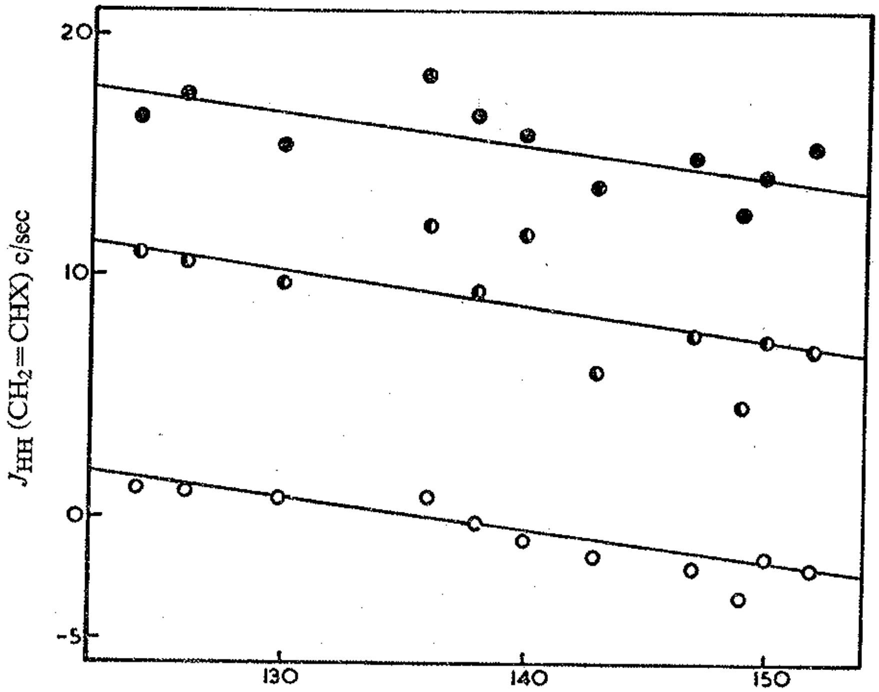

FIG. 5.—The relation between J_{CH} observed in CH_3X and J_{HH} observed in CH_2=CHX. The three sets of points are for J_{trans}^{HH}, J_{cis}^{HH} and J_{gem}^{HH}, from top to bottom.

RELATION OF J_{CH} TO J_{vic}^{HH} AND J_{gem}^{HH}

Both J_{CH} and J_{HH} in hydrocarbons depend upon the electron density at the proton and on the carbon orbital hybridization so one would expect there to be some relation between the coupling constants. Such a relation is implicit in the fact that $J_{CH}(CH_3X)$[17] and $J_{HH}(CH_2{=}CHX)$,[6, 18, 19] cis, trans and geminal, individually have an approximately linear dependence on the electronegativity of X. This may be seen in fig. 5, where the three proton-proton coupling constants observed in a number of substituted ethylenes are plotted against the corresponding $J_{CH}(CH_3X)$. The scatter is considerable but there is nonetheless a general linear correlation between J_{CH} and each of the three types of J_{HH}. It is noteworthy that the scatter comes mainly from the J_{CH} values, which indicates that there are interactions affecting J_{CH} which do not contribute significantly to J_{HH}.

Another point of interest is that all three types of J_{HH} increase while J_{CH} decreases, based upon the arbitrary assignment of J_{trans}^{HH} as positive. A decrease in J_{CH} implies a decrease in the s character of the C—H bond. In turn, this would tend to decrease the C—C—H bond angle. And, according to valence bond calculations of J_{HH} in the HCCH fragment,[3] this would increase both J^{HH}_{cis} and J^{HH}_{trans}, as observed. It is surprising to find virtually the same dependences upon J_{CH} for all three types of J_{HH} in spite of the different structural features and magnitudes involved, particularly for J^{HH}_{gem}. These similar slopes in fig. 5 may be accidental; nonetheless they are one of many features of internuclear coupling which remain to be explained.

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