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Valence-Bond Studies of the Dependence upon Substituents of C^{13}–H and Si^{29}–H Coupling*

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An interpretation is presented for the additivity of substituent effects on the C^{13}–H coupling constant, which has been observed previously in the high-resolution NMR spectra of substituted methanes. Each atom or group X is assigned a characteristic "affinity" for *s* character in the carbon hybrid orbital of the C–X bond. Distribution of *s* character among the carbon orbitals in accord with the relative *s* affinities of the four substituents leads to the observed additivity relation 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 the C–H bond (α_H^2) and the observed C^{13}–H coupling constant ($J_{CH}=500\,\alpha_H^2$). Also, it allows the determination of the *s* character of the other carbon orbitals. The dependence of the *s* character of the C–X bond on the electronegativity of X is discussed in terms of electron spin and charge correlation. It is noted that the hybridization changes should affect not only J_{CH} but also J_{HH}, which is consistent with the observed proportionality between $J_{CH}(CH_3X)$ and the *cis* and *trans* H–H coupling constants in $CH_2{=\!=}C^{13}HX$.

The treatment developed for methanes has been extended to J_{CH} in substituted ethylenes and to the Si^{29}–H coupling in silanes. For the former, introduction of the *s*-electron affinities, obtained from the values of $J_{CH}(CH_3X)$ observed for the substituted methanes, leads to the result that $J_{CH}(CH_2{=\!=}C^{13}HX)=J_{CH}(CH_2{=\!=}CH_2)+\frac{4}{3}[J_{CH}(CH_3X)-J_{CH}(CH_4)]$. Values predicted in this manner are systematically larger than those observed, which implies that there is a small, ***negative*** π-electron contribution of 5 to 10 cps to $J_{CH}(CH_2{=\!=}C^{13}HX)$. Such a contribution is compatible with current theories for proton and C^{13} hyperfine splittings in ESR spectra of free radicals. The Si^{29}–H coupling constants observed in substituted silanes exhibit large, systematic deviations from the simple additivity found in the methanes. These deviations are explicable qualitatively in terms of changes in the Si–H-bond polarity.

I. INTRODUCTION

In earlier work,[1–3] the C^{13}–H spin–spin coupling constant (J_{CH}) found in high-resolution nuclear magnetic resonance spectra has been related to the parameters used in describing the C–H bond, namely the carbon orbital hybridization and the coefficient λ of the ionic term. The mathematical form of the valence-bond equation for J_{CH} is such that increasing λ decreases J_{CH}. However, the observed trend[2] appears to be the opposite; that is, compounds in which λ is expected to be large because of electronegative substituents have large values of J_{CH} rather than small. Muller[2] called attention to this fact and concluded that the dependence of J_{CH} on the *s* character of the carbon orbital used in forming the C–H bond predominates over the dependence of J_{CH} on the C–H-bond polarity. This is shown to be so in the present paper by a calculation of the explicit dependence of J_{CH} on λ and *s* character. We find, by means of the valence bond approach used by Karplus and Grant,[4] that J_{CH} is relatively insensitive to the value of λ, within certain limits, and directly proportional to the *s* character.

This finding is basic to an analysis of the empirical linear additivity of group contributions to J_{CH} in substituted methanes, which is our main concern. Malinowski[5] reported that the C^{13}–H coupling constant observed in compounds of the form CHXYZ was expressible to a very good approximation as:

$$J_{CH}(CHXYZ)=\zeta_X+\zeta_Y+\zeta_Z, \qquad (1)$$

where ζ_X, the contribution of group X to J_{CH}, is defined from experiment by the relations

$$\zeta_H=\tfrac{1}{3}J_{CH}(CH_4)$$

and

$$\zeta_X=J_{CH}(CH_3X)-2\zeta_H. \qquad (2)$$

This is only one of several equivalent forms[6] in which the additivity may be expressed, all stemming from the basic, empirical relationship,

$$J_{CH}(CHXYZ)=J_{CH}(CH_3X)+J_{CH}(CH_3Y)+J_{CH}(CH_3Z)-2J_{CH}(CH_4). \qquad (3)$$

Spin–spin coupling constants have been shown to depend mainly on the Fermi contact term for the C^{13}–H group.[1] Furthermore, for coupling between directly bonded atoms, deviations from perfect pairing are not important.[1] Using these approximations and a simple model, we have been able to derive Eqs. (1) and (3) describing the observed linear additivity of group contributions to C^{13}–H coupling constants in the substituted methanes. Also, as mentioned in a preliminary account of this work,[7] the analysis has been extended to J_{CH} in substituted ethylenes and it enables values of $J_{CH}(CH_2{=\!=}C^{13}HX)$ to be predicted from those

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* Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. The work was also supported by the Office of Naval Research.

[1] M. Karplus and D. M. Grant, Proc. Natl. Acad. Sci. U. S. **45,** 1269 (1959). See also H. S. Gutowsky, D. W. McCall, and C. P. Slichter, J. Chem. Phys. **21,** 279 (1953), for an earlier discussion of the coupling of directly bonded nuclei and its dependence upon the perfect pairing structure.

[2] N. Muller and D. Pritchard, J. Chem. Phys. **31,** 768, 1471 (1959); N. Muller, *ibid.* **36,** 359 (1962).

[3] J. Shoolery, J. Chem. Phys. **31,** 1427 (1959).

[4] Karplus and Grant,[1] have given general expressions for J_{CH}. We proceed from there to illustrate the explicit dependence of J_{CH} on λ and *s* character.

[5] E. Malinowski, J. Am. Chem. Soc. **83,** 4479 (1961).

[6] We thank Dr. T. H. Brown for discussion leading to this conclusion. One other equivalent form is $J_{CH}(CHXYZ)=\zeta_H'+\zeta_X'+\zeta_Y'+\zeta_Z'$, where $\zeta_X'=J_{CH}(CH_3X)-\frac{3}{4}J_{CH}(CH_4)$.

[7] H. S. Gutowsky and C. S. Juan, J. Am. Chem. Soc. **84,** 307 (1962).

observed for $J_{CH}(CH_3X)$. However, the predicted values are systematically somewhat (5 to 10 cps) larger than those observed (150 to 200 cps). If, as seems likely, these discrepancies result from *negative* π-electron contributions to J_{CH}, they may provide useful information on σ–π interactions and hyperfine constants in free radicals. Also, we consider the Si^{29}–H coupling constant J_{SiH} in the substituted silanes, to which the additivity rule does not apply.[7] At first we thought this might be due to the use of *d* electrons in the silicon bonding orbitals. However, since then, a more detailed analysis indicates that the deviations from additivity result largely from changes in polarity of the Si–H bond. Finally, as discussed elsewhere,[8] if our model is correct for the effect of X upon J_{CH} in CH_3X or $CH_2{=}CHX$ molecules, it should lead to a better understanding of substituted effects upon J_{HH}, because the latter also is affected by hybridization of orbitals in the C–H bonds. In fact, the hybridization changes which appear to dominate J_{CH} are consistent, at least semiquantitatively, with the observed dependences of $J_{cis}{}^{HH}$ and $J_{trans}{}^{HH}$ upon the substituent in $CH_2{=}CHX$.

II. VALENCE-BOND FORMULATION FOR SUBSTITUTED METHANES

General Treatment

The coupling constant $J_{NN'}$ for a pair of nuclei N and N' may be calculated by second-order perturbation theory using the Hamiltonian given by Ramsey.[9] The expression for $J_{NN'}$ consists of several terms; however, in this paper we are concerned only with the Fermi contact term which has been shown[1] to be the dominant term for the C^{13}–H coupling:

$$J_{CH} \approx (J_{CH})_{\text{contact}} = \frac{-2}{3h\Delta E}\left(\frac{16\pi\beta\hbar}{3}\right)^2 \times \gamma_C\gamma_H \Big(\Psi_0 \Big| \sum_{k,j} \delta(\mathbf{r}_{kC})\,\delta(\mathbf{r}_{jH})\,\mathbf{S}_k\cdot\mathbf{S}_j \Big| \Psi_0\Big). \quad (4)$$

The symbols used above have their standard meanings. The perfect pairing approximation may be used for the ground-state wavefunction Ψ_0 since for electron-spin interactions between bonded atoms deviations from perfect pairing are not important.[1,10] We use the separated electron-pair wavefunction,

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

where

$$\psi_r(i,j) = u_r(i,j)\{[\alpha(i)\beta(j) - \beta(i)\alpha(j)]/\sqrt{2}\} \quad (6)$$

and $u_r(i,j)$ is taken to be of the valence-bond form with inclusion of ionic terms

$$u_1(1,2) = \eta_1[\phi_a(1)\phi_x(2) + \phi_a(2)\phi_x(1) + \lambda_a\phi_a(1)\phi_a(2) + \lambda_x\phi_x(1)\phi_x(2)]. \quad (7)$$

In the latter ϕ_a, ϕ_b, ϕ_c, and ϕ_d are carbon atomic orbitals; ϕ_x, ϕ_y, ϕ_z, and ϕ_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 Eq. (4) and using the Dirac identity $\mathbf{S}_k\cdot\mathbf{S}_j = \frac{1}{4}(2P_{kj}{}^s - 1)$, in which $P_{kj}{}^s$ is an operator interchanging the spins of electrons k and j, one obtains

$$J_{CH} = \frac{\gamma_C\gamma_H}{h\Delta E}\left(\frac{16\pi\beta\hbar}{3}\right)^2 \eta^2 (\phi_d \,|\, \delta(\mathbf{r}_{iC}) \,|\, \phi_d) \times (\phi_h \,|\, \delta(\mathbf{r}_{jH}) \,|\, \phi_h). \quad (8)$$

We assume carbon hybrid orbitals formed from one $2s$ orbital and three $2p$ orbitals; e.g., for the C–H bond,

$$\phi_d = \alpha_H s + (1-\alpha_H{}^2)^{\frac{1}{2}} p_\sigma. \quad (9)$$

$\alpha_H{}^2$ is commonly called the *s* character of the carbon hybrid orbital. The p_σ's are linear combinations of p_x, p_y, and p_z orbitals and are oriented along different directions in space. In general, $\alpha_{X,Y,\text{ or }Z}$ will depend on the group or atom X, Y, or Z bonded to the carbon. Substituting ϕ_d and $\phi_h \equiv 1s_H$ into Eq. (8), one finds that

$$J_{CH} = (\gamma_C\gamma_H/h\Delta E)(\tfrac{16}{3}\pi\beta\hbar)^2\eta^2\alpha_H{}^2\,|2s_C(0)|^2\,|1s_H(0)|^2, \quad (10)$$

where

$$\eta^{-2} = \{2 + (2+\lambda_C\lambda_H)[\alpha_H{}^2 S_{1s2s}{}^2 + (1-\alpha_H{}^2) S_{1s2p}{}^2 + 2\alpha_H(1-\alpha_H{}^2)^{\frac{1}{2}} S_{1s2s} S_{1s2p}] + 4(\lambda_C+\lambda_H) \times [\alpha_H S_{1s2s} + (1-\alpha_H{}^2)^{\frac{1}{2}} S_{1s2p}] + \lambda_C{}^2 + \lambda_H{}^2\}, \quad (11)$$

$2s_C(0)$ is the $2s$ wavefunction of carbon evaluated at the carbon nucleus, and $1s_H(0)$ is the corresponding quantity for the hydrogen $1s$ function. S_{1s2s} and S_{1s2p} are the overlap integrals between the hydrogen $1s$ atomic orbital and the respective carbon atomic orbitals. In Eq. (11) for η^{-2}, λ_H is much less than λ_C and can be neglected, because the electronegativity of C is greater than that of H. Also, Eqs. (7) and (11) are symmetrical in λ_C and λ_H, so the coefficient of the ionic contribution to the wavefunction is hereafter denoted by λ_{C-H}.

Equation (10) leads to

$$J_{CH} = (A\eta^2/\Delta E)\alpha_H{}^2 \equiv J_0\alpha_H{}^2 \text{ cps}, \quad (12)$$

where A is a collection of constants, and J_0 is 500 cps, as determined from the observed value[1,2] of 125 cps for $J_{CH}(CH_4)$. This value for J_0 is consistent with the valence-bond theory inasmuch as Karplus and Grant[1] obtained a reasonable value of 0.374 for λ_{C-H}, using the same approach, with $J_{CH} = 124$ cps, in combination

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[8] H. S. Gutowsky and C. S. Juan, Discussions Faraday Soc. **34**, (in press) (1962).

[9] N. F. Ramsey, Phys. Rev. **91**, 303 (1953).

[10] For $CH_4\Psi_0 = 1.08\,\psi_1 + 0.001\,\psi_2 - 0.028\,\psi_3$, where ψ_1 is the perfect pairing structure, and ψ_2 and ψ_3 are nonperfect pairing terms [M. Karplus and D. H. Anderson, J. Chem. Phys. **30**, 6 (1959)]. Although ψ_2 and ψ_3 account for $J_{HH'}$, they are not important in J_{CH}.

TABLE I. The calculated dependence[a] upon s character of the normalization constant $\eta^2(\lambda_{C-H}, \alpha_H)$, defined in Eq. (11) for the valence bond function describing the C–H bond.

α_H^2	η^2	α_H^2	η^2
0.2400	0.2419	0.3600	0.2395
0.2600	0.2412	0.3800	0.2394
0.2800	0.2407	0.4000	0.2393
0.3000	0.2403	0.4200	0.2394
0.3200	0.2399	0.4400	0.2395
0.3400	0.2397	0.4500	0.2396

[a] Calculated using $\lambda_{C-H}=0.374$ and overlap integrals from reference 11.

with an estimate of ΔE and calculations of the overlap integrals from Hartree–Fock functions. We have obtained virtually identical results using Kotani's tables[11] for the integrals.

Dependence of J_{CH} upon ΔE, λ_{C-H} and α_H^2

Although Eq. (12) was derived for J_{CH} in substituted methanes, it applies in general to directly bonded nuclei for which the σ electron, Fermi contact term is dominant. Moreover, depending upon the sensitivity of ΔE and η^2 to substituents, it affords an attractive semiempirical 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 the ΔE pertinent to Eq. (12) to be very nearly constant. This follows from the fact that ΔE is approximately twice the bond energy,[1] which varies by only a few percent for C–H bonds.

Such an easy semiquantitative generalization can not be made for η^2 because of its complex dependence on λ, α^2, and the overlap integrals, which differ with the atomic species in the bond and also with the substituents. However, these dependences can be calculated relatively simply and directly. For the C–H bond, $\eta^2(\lambda_{C-H}, \alpha_H)$ was found to be relatively insensitive to the value of α_H, as shown in Table I. η^2 changes very slowly with α_H^2 and goes through a minimum at $\alpha_H^2=0.400$. The total change in η^2 over the entire range of values of α_H^2 of interest here is only 0.2%. η^2 is also relatively insensitive to λ_{C-H} as discussed in the following paragraph.

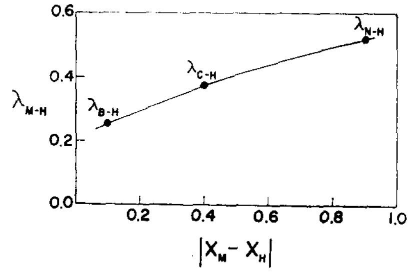

FIG. 1. The M–H "bond polarity parameter," λ_{M-H} in MH_4, and its dependence upon the difference in electronegativities $|X_M - X_H|$ of M and H. The empirical λ_{M-H} values are from reference 1 and the electronegativities from Pauling.

Electron-withdrawing substituents are expected to increase electronegativity of the C atom by about 0.1 to 0.2 units according to estimates of effective electronegativities by proton chemical-shift measurements.[12] From the empirical values of λ_{B-H}, λ_{C-H}, and λ_{N-H} given by Karplus and Grant,[1] and plotted in Fig. 1,[13] it is apparent that an increase in electronegativity of the carbon by 0.2 units would change λ_{C-H}, from 0.374 to about 0.44. The dependence of η^2 on λ_{C-H}, contained in Eq. (11), was demonstrated by Karplus and Grant[1] and is shown in Fig. 2. From Fig. 2 we find that the estimated increase in λ_{C-H} with the most electronegative substituents decreases η^2 to about $0.95\eta^2(CH_4)$. However, such an increase in λ_{C-H} is accompanied by an increase in Z_{eff} for the $2s$ and $2p$ electrons of carbon which leads to a decrease in the overlap integrals S_{1s2s}, S_{1s2p}, and to an increase in η^2. Therefore, the effects tend to cancel, and even though α_H, 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 $J_0 \cong 500$ cps and to the conclusion that J_{CH} is linearly proportional to α_H^2, the s character of the carbon orbital in the C–H bond.

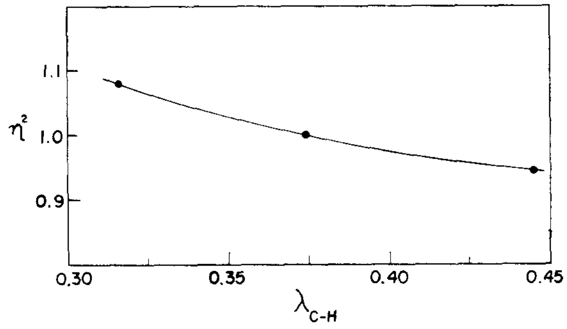

FIG. 2. Variation of the normalization constant η^2, in units of $\eta^2(CH_4)$, with the C—H bond polarity parameter λ_{C-H}. These values are from reference 1 for $\alpha_H^2=0.25$.

Derivation of the Additivity Relation

Two additional assumptions are required to derive the additivity relation observed by Malinowski.[5] The first is that *one* carbon $2s$ orbital is used in forming the

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[11] M. Kotani, A. Amemiya, E. Ishiguro, and T. Kimura, *Table of Molecular Integrals* (Maruzen and Company, Tokyo, 1955).

[12] B. Dailey and J. Shoolery, J. Am. Chem. Soc. 77, 3977 (1955).

[13] The electronegativity of B is less than that of H. Hence, the coefficient of the $\phi_H(1)\phi_H(2)$ term (λ_H) is much larger than the coefficient of the $\phi_B(1)\phi_B(2)$ term (λ_B) so that λ_B is neglected and λ_H is plotted as λ_{B-H}. In the case of C–H and N–H, the electronegativities of C and N are greater than that of H so that λ_H is neglected and λ_C and λ_N are plotted as λ_{C-H} and λ_{N-H}. The Si–H case is similar to that of B–H.

C–H, C–X, C–Y, and C–Z bonds. In this case, α_X, α_Y, α_Z, and α_H are related by

$$\alpha_X^2+\alpha_Y^2+\alpha_Z^2+\alpha_H^2=1. \qquad (13)$$

The second concerns the manner in which the 2*s* orbital is distributed among the four bonds. We present a simple model for this, the physical basis of which is explained later.

A substituent may prefer bond formation with a carbon hybrid orbital having more or less *s* character than the normal sp^3 value of $\frac{1}{4}$. If so, substituents may be arranged in their order of "affinity for *s* character," analogous to the way in which elements are arranged in the electromotive series or electronegativity scale. Let Δ_X be a measure of the "affinity" of substituent X for carbon 2*s* character; further, let Δ_X be measured with respect to H such 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 as shown diagrammatically in Fig. 3. The difference between the depths of the wells for X and H is defined as Δ_X. The 2*s* character distributes 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 Eq. (13), 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. In CH_3X, since the H wells are deeper than that of X by the amount Δ_X, then an H well in CH_3X has $\frac{1}{4}\Delta_X$ 2*s* character more than an H well in CH_4. In general, the H well in CHXYZ has $[\frac{1}{4}\Delta_X+\frac{1}{4}\Delta_Y+\frac{1}{4}\Delta_Z]$ 2*s* character more than an H well in CH_4. Expressed mathematically, this means that for CH_3X

$$\alpha_H^2(CH_3X)=\alpha_H^2(CH_4)+\tfrac{1}{4}\Delta_X, \qquad (14)$$

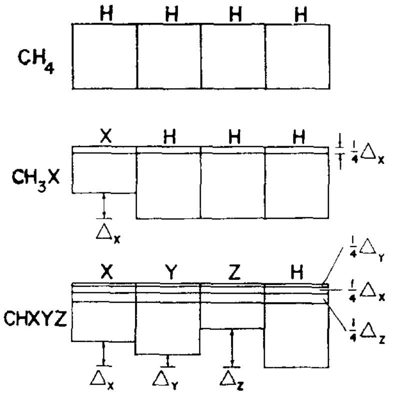

FIG. 3. A diagram of the model used in deriving the additivity relation for the effects of substituents upon J_{CH}(CHXYZ). The vertical lines enclose the four interconnected potential wells for the 2*s* electrons; these are the four bonding orbitals of the carbon atom.

TABLE II. Substituent parameters Δ_X obtained[a] from values of C^{13}—H coupling constants observed in some CH_3X compounds.

CH_3X	$J_{CH}(CH_3X)$[b] (cps)	α_H^2	Δ_X
$Al_2(CH_3)_6$	113	0.226	−0.096
$Si(CH_3)_4$	118	0.236	−0.056
$(CH_3)_3SiCN$	122	0.244	−0.024
$CH_3C(CH_3)_3$	124	0.248	−0.008
CH_4	125	0.250	0.000
CH_3COCH_3	126	0.252	+0.008
CH_3CH_3	126	0.252	+0.008
CH_3CHCH_3Br	126[c]	0.252	+0.008
$CH_3\phi$	126	0.252	+0.008
CH_3CHO	127	0.254	+0.016
CH_3CH_2Br	128[c]	0.256	+0.024
CH_3CH_2Cl	128[c]	0.256	+0.024
CH_3COOH	130	0.260	+0.040
CH_3CHCl_2	131[c]	0.262	+0.048
$CH_3N(CH_3)_2$	131	0.262	+0.048
CH_3CH_2I	132[c]	0.264	+0.056
CH_3NHCH_3	132	0.264	+0.056
$CH_3C{\equiv}CH$	132	0.264	+0.056
CH_3NH_2	133	0.266	+0.064
CH_3CCl_3	134	0.268	+0.072
CH_3CN	136	0.272	+0.088
$(CH_3)_2NCHO$	138	0.276	+0.104
CH_3SH	138	0.276	+0.104
$(CH_3)_2S$	138	0.276	+0.104
CH_3SOCH_3	138	0.276	+0.104
CH_3OH	141	0.282	+0.128
$CH_3O\phi$	143	0.286	+0.144
$(CH_3O)_2CO$	147	0.294	+0.176
CH_3F	149	0.298	+0.192
CH_3Cl	150	0.300	+0.200
CH_3I	151	0.302	+0.208
CH_3Br	152	0.304	+0.216

[a] Δ_X was calculated using Eq. (14) with values of α_H^2 obtained from $J_{CH}(CH_3X)$ by means of Eq. (12). In the latter, J_0 was given by $J_{CH}(CH_4)=\frac{1}{4}J_0=125$ cps.

[b] Taken from reference 2 unless otherwise specified.

[c] Taken from reference 5.

and for CHXYZ,

$$\alpha_H^2(CHXYZ)=\alpha_H^2(CH_4)+\tfrac{1}{4}\Delta_X+\tfrac{1}{4}\Delta_Y+\tfrac{1}{4}\Delta_Z. \qquad (15)$$

Eliminating Δ_X, Δ_Y, and Δ_Z from Eq. (15), with Eq. (14) and similar equations for Y and Z, we obtain

$$\alpha_H^2(CHXYZ)=\alpha_H^2(CH_3X)+\alpha_H^2(CH_3Y)+\alpha_H^2(CH_3Z)-2\alpha_H^2(CH_4). \qquad (16)$$

TABLE III. A comparison of α_H^2, in CHXYZ, obtained directly from the observed values of J_{CH}(CHXYZ) by the relation $\alpha_H^2 = J_{CH}/J_0$ and from the additivity of the substituent effects, $\alpha_H^2(\text{CHXYZ}) = \frac{1}{4}(1+\Delta_X+\Delta_Y+\Delta_Z)$.

CHXYZ	J_{CH}[a] (cps)	α_H^2(CHXYZ) J_{CH}/J_0[b]	α_H^2(CHXYZ) $\frac{1}{4}(1+\Delta_X+\Delta_Y+\Delta_Z)$	Difference
$\phi CH_2\phi$	127	0.254	0.254	0.0
$CH_2(COOH)_2$	132[c]	0.264	0.270	+0.006
$CH_2(CN)_2$	145[c]	0.290	0.294	+0.004
$CH_3C^{13}H_2I$	149	0.298	0.304	+0.006
$CH_3C^{13}H_2Br$	151	0.302	0.306	+0.004
$(CH_3)_2C^{13}HBr$	151	0.302	0.308	+0.006
ϕCH_2Cl	152	0.304	0.302	−0.002
ϕCH_2Br	153	0.306	0.306	0.0
$ClCH_2CH_2Cl$	154	0.308	0.306	−0.002
$BrCH_2CH_2Br$	157	0.314	0.310	−0.004
CH_2ClCN	161	0.322	0.322	0.0
CH_2I_2	173	0.346	0.354	+0.008
CH_2Br_2	178	0.356	0.358	+0.002
CH_2Cl_2	178	0.356	0.350	−0.006
$Cl_2CHCHCl_2$	182	0.364	0.362	−0.002
CH_2F_2	185[c]	0.370	0.346	−0.024
$CHCl_2CN$	189	0.378	0.372	−0.006
$CHBr_3$	206[c]	0.412	0.412	0.0
$CHCl_3$	209[c]	0.418	0.400	−0.018

[a] These observed values were obtained from reference 5, or from references therein, unless otherwise specified.

[b] Calculated using $J_0 = 4J_{CH}(CH_4) = 500$ cps.

[c] From reference 2.

Equation (16) may be rearranged to give

$$\alpha_H^2(\text{CHXYZ}) = [\alpha_H^2(\text{CH}_3\text{X}) - \tfrac{2}{3}\alpha_H^2(\text{CH}_4)] + [\alpha_H^2(\text{CH}_3\text{Y}) - \tfrac{2}{3}\alpha_H^2(\text{CH}_4)] + [\alpha_H^2(\text{CH}_3\text{Z}) - \tfrac{2}{3}\alpha_H^2(\text{CH}_4)].$$

And by means of Eq. (12) this leads to

$$J_{CH}(\text{CHXYZ}) = \zeta_X + \zeta_Y + \zeta_Z, \qquad (1)$$

which is exactly the form of additivity observed by Malinowski.[5] Equation (16) may also be combined with Eq. (12) to give Eq. (3) and to lead to the other forms[6,8] of the additivity relation.

Discussion

The valence bond approach gives a direct relation between the s character of the carbon orbital involved in the C–H bond in substituted methanes and the C^{13}-H coupling constant. The s character of the carbon orbital in the C–X bond may also be obtained with the use of Eq. (13) for CH_3X, CH_2X_2, and CHX_3; and in general, according to the model presented here,

$$\alpha_X^2(\text{CHXYZ}) = \tfrac{1}{4}(1+\Delta_X+\Delta_Y+\Delta_Z) - \Delta_X, \qquad (17)$$

as shown graphically in Fig. 3. The values of Δ_X for a number of substituents are given in Table II. These values exhibit an interesting relation between the s electron affinity Δ_X and the electronegativity of substituent X, with the Δ_X being small for electropositive substituents (−0.096 for Al) and large for electronegative (+0.2 for the halogens). In addition, Table III shows that the effects of substituents upon α_H^2 are additive to within an accuracy of 2% for about 20 polysubstituted methanes. The additivity can be expressed in terms of J_{CH} by taking the product of α_H^2 and J_0, with a value of 500 cps for the latter.

The model presented here may seem somewhat arbitrary at first glance. But at least one of its main aspects, the relation between Δ_X and the electronegativity of X, can be explained qualitatively as a simple consequence of electron correlation effects. Apart from charge correlation, i.e., the tendency for all electrons to keep apart from each other because of Coulombic repulsion, there is spin correlation, which arises as a result of the Pauli principle. Electrons having the same spin have a low probability of being near one another while those having opposed spins have no tendency to keep apart in this way. Consider the C^{4-} ion. Because of charge and spin correlation of the 8 L-shell electrons, a configuration of four pairs arranged tetrahedrally has the highest probability.[14] Methane can be pictured as formed from C^{4-} by attaching four protons and it is at equilibrium in a regular tetrahedral configuration. The electron distribution is most conveniently described in terms of sp^3 hybrid orbitals on the carbon.

Now suppose we attach two protons and two X^+

TABLE IV. Dependence of Δ_X on electronegativity and number of lone pair electrons of first atom in the substituent X.

First atom of X	No. of comp.	J_{CH}[a] range (cps)	J_{CH} av (cps)	Δ_X av	Pauling electroneg.
Al	1	113	113	−0.096	1.5
Si	2	118–122	120	−0.040	1.8
H	1	125	125	0.0	2.1
C	23	124–136	129	+0.032	2.5
N	11	131–139	137	+0.096	3.0
S	4	138–140	138.5	+0.108	2.5
O	8	141–147	144	+0.152	3.5
Halogen	4	149–152	150.5	+0.204	2.2–4.0

[a] From reference 2; E. Snyder and J. D. Roberts, J. Am. Chem. Soc. **84**, 1582 (1962); P. C. Lauterbur, J. Chem. Phys. **26**, 217 (1957).

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[14] P. G. Dickens and J. W. Linnett, Quart. Revs. (London) **11**, 291 (1957).

to C^{4-}, where X is a substituent with electronegativity greater than that of hydrogen It is to be expected that the two bonding pairs to X will be "centered" farther from the carbon nucleus than the two bonding pairs to H. Consequently, the four pairs will no longer tend to be oriented in the form of a regular tetrahedron but both spin and charge correlation would cause the angle subtended by the bonding pairs between C and X to be less than that subtended by the bonding pairs between C and H. The electron distribution can then be described by nonequivalent hybrids with greater *s* character in the C–H bonds and less *s* character in the C–X bonds than the equivalent hybrids in methane. Or, in terms of the parameter introduced here, Δ_X would be positive as observed.

On the other hand, for a substituent X whose electronegativity is less than H, the two bonding pairs to H will be "centered" farther from the carbon nucleus than the two bonding pairs to X. Consequently, the electron distribution can be described by hybrids with greater *s* character in the C–X bonds than in the C–H bonds, or by a negative Δ_X. The greater the difference between the electronegativity of X and H is, the more enhanced is this effect, i.e., Δ_X is a larger number. Therefore, Δ_X is a characteristic of an atom or group X and depends on the algebraic difference between the electronegativity of X and H.[15] This is shown clearly by the summary of Δ_X values in Table IV.

Also, the latter reveals the importance of another factor. When X possesses lone-pair electrons there are interactions between the lone pairs and the electrons of the other substituents and a possibility of multiple bonds, so that Δ_X depends upon the electron pairs of the substituent as well as upon its electronegativity. This is apparent in Table IV, where it may be seen that for substituents with the same electronegativity Δ_X tends to be greater for those which have the greater number of lone-pair electrons.

A less satisfactory feature of our results is their relation to observed bond angles. The "interorbital" angles (angles between the symmetry axes of the carbon hybrid orbitals) corresponding to the hybridization parameters obtained from J_{CH} data are compared with observed bond angles (angles between the lines joining the bonded nuclei) in Table V. We note that the H—C—X angles observed for CH_3X are less than tetrahedral in spite of the fact that X is bigger than H. This is clearly due to the effect described above. Nonethelesss, all of the observed H—C—X and X—C—X angles are significantly greater than the angles calculated from α_H^2 and α_X^2, assuming orbital following. This difference seems to increase with increasing size of X and is greater for CH_2X_2 (∼12°) than for CH_3X (∼5°), presumably due to steric interactions.

TABLE V. "Interorbital" angles calculated from α_H^2 and α_X^2 for halomethanes, and their comparison with the observed bond angles.

X	H—C—X angle in CH_3X Calc.	Obs.[a]	Diff.	X—C—X angle in CH_2X_2 Calc.	Obs.[b]	Diff.
I	102.2°	106.9°	4.7°	100.5°	114.7°	14.2°
Br	101.8	107.3	5.5	99.7	112±2	∼12
Cl	102.6	108.0	5.4	99.7	111.8	12.1
F	103.0	108.5	4.5	98.5	108.3	9.8

[a] C. Costain, J. Chem. Phys. **29**, 864 (1958).

[b] *Interatomic Distances*, edited by L. E. Sutton (The Chemical Society, London, 1958); H. A. Levy and L. O. Brockway, J. Am. Chem. Soc. **59**, 1662 (1937); R. J. Myers and W. D. Gwinn, J. Chem. Phys. **20**, 1420 (1952).

The incompatibility of α_H^2 hybridization parameters obtained previously from J_{CH} data with the observed bond angles has been discussed by Muller.[2] He invoked "bent bonds" to explain differences found for the methyl halides. However, high-resolution microwave studies made recently by Flygare *et al.*[16] rule out bent C–Cl bonds in compounds where they were long believed to be present. So it seems unlikely that differences given in Table V result from "bent bonds." Furthermore, the plot of α_H^2 vs "interorbital" angles is almost a perfectly straight line, especially in the region of values of α_H^2 encountered here so that vibrational averaging[17] of the C–H coupling constant assuming orbital following[18] yields the same value as for the "static" equilibrium configuration. So the discrepancies can not be attributed to vibrational averaging effects. Quite apart from the relationship derived here between hybridization and J_{CH}, the bond angles in CH_2Cl_2, 1,1-dichlorocyclopropane and other molecules can not be reconciled with any carbon hybrid orbitals built only from *s* and *p* functions. The problem, therefore, is of a more general nature and does not arise simply from the approximations used in the expression for J_{CH}.

In closing this discussion of results for the substituted methanes, we wish to amplify on our earlier statement[7] that a simple molecular orbital formulation gives results equivalent to the valence bond treatment presented above. A two-center molecular orbital of the form,

$$\psi = c_1(1s_H) + c_2(2s_C) + c_3(2p_{\sigma C}),$$

yields essentially the same equation as Eq. (12). The main difference is the normalization constant, which now depends upon the coefficients c_1, c_2, and c_3. However, these coefficients define the amount of carbon 2*s* orbital involved in and the polarity of the C–H bond; and the normalization constant for the molecular orbital

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[15] We are indebted to a referee for pointing out that a similar idea has been advanced by H. A. Bent, Chem. Revs. **61**, 275 (1961).

[16] W. H. Flygare, A. Narath, and W. D. Gwinn, J. Chem. Phys. **36**, 200 (1962); W. H. Flygare and W. D. Gwinn, *ibid.* **36**, 787 (1962).

[17] This was approximated for $J_{gem}^{HH'}$ by H. S. Gutowsky, V. D. Mochel, and B. G. Somers, J. Chem. Phys. **36**, 1153 (1962).

[18] J. W. Linnett and P. J. Wheatley, Trans. Faraday Soc. **45**, 33, 39 (1949).

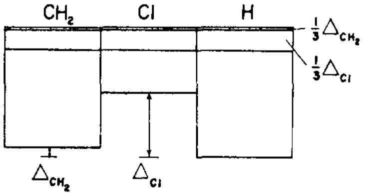

FIG. 4. A diagram of the model used in extending the treatment of substituent effects from methanes to ethylenes ($CH_2=C^{13}HX$). The vertical lines enclose the three σ-bonding orbitals of the carbon atom in the $C^{13}HX$ group. In a planar sp^2 $C^{13}H_3$ radical, the three potential wells would be of the same depth and equally occupied by the 2*s* electrons. Δ_{CH_2} and Δ_{Cl} represent the different *s* electron affinities of the $CH_2=C^{13}$ and $C^{13}-Cl$ σ bonds in $CH_2=C^{13}HX$, which lead to the redistribution, among the three σ bonds, of the *s* character indicated by the horizontal lines at the top.

equivalent of Eq. (12) is no more sensitive to changes in these parameters than we found in the valence bond analysis. The model leading from Eq. (12) to Eqs. (1), (3) and (15) to (17) is the same for both approaches. Finally, we wish to point out that the valence bond treatment given below in Sec. III for substituted ethylenes and acetylenes may be formulated as well in terms of the two-center molecular orbital.

III. SUBSTITUTED ETHYLENES AND ACETYLENES

The treatment carried out for the methanes may be extended (with some reservation) to the σ electron contribution to J_{CH} in sp^2 and sp hybridized carbon. Equation (10) applies to the latter, subject to the same approximations. Using $\lambda_{C-H}=0.374$ and the overlap integrals[11] appropriate to the C–H bond distances in ethylene and acetylene, we find η^2 for these two compounds to be $0.987\eta^2(CH_4)$ and $0.977\eta^2(CH_4)$, respectively. Moreover, $\eta^2/\Delta E$ for ethylene and acetylene is affected no more by substituent effects, i.e., by changes in $\alpha_H{}^2$, bond polarity and bond strength, than 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. Because of this, the model developed for the effects of substituents on $J_{CH}(CHXYZ)$ should apply to ethylenes as well.

Calculation of $J_{CH}(CH_2=C^{13}HX)$ from Δ_X for CH_3X

The main difference encountered in extending the treatment of substituent effects in the methanes to the ethylenes is that there are three 2*s* wells instead of four. In ethylene itself the first two are identical H wells and the third differs in depth from these two by Δ_{CH_2}, where the subscript denotes the doubly bonded group, $CH_2=$. In substituted ethylenes all three wells are of different depths, as shown in Fig. 4. Following our previous arguments that Δ_X depends mainly on the difference in electronegativity of X and H, we should expect the same values for Δ_X in the ethylenes as in the methanes. The value for Δ_{CH_2} (ethylenes) is taken as equal to Δ_{CH_3} (methanes), i.e., +0.008, since the "substituent" CH_2 in the ethylenes has no direct counterpart in the methanes. For the same reason, the values for Δ_{CHX}, Δ_{CXY}, and Δ_{CX_2} are taken to be equal to Δ_{CH_2X}, Δ_{CHXY}, and Δ_{CHX_2} respectively.

On this basis the *s* character for a monosubstituted ethylene is given by

$$\alpha_H{}^2(CH_2=C^{13}HX)=\tfrac{1}{3}[1+\Delta_{CH_2}+\Delta_X]$$
$$=\alpha_H{}^2(CH_2=CH_2)+\tfrac{1}{3}\Delta_X, \quad (18)$$

which with Eq. (12) gives rise to

$$J_{CH}(CH_2=C^{13}HX)=J_{CH}(CH_2=CH_2)$$
$$+\tfrac{4}{3}[J_{CH}(CH_3X)-J_{CH}(CH_4)]. \quad (19)$$

A comparison of Eq. (18) for $CH_2=C^{13}HX$ with Eq. (14) for CH_3X shows that X causes a change in $\alpha_H{}^2$ and in J_{CH}, which in the ethylene is $\frac{4}{3}$ that in the methane. This is because the substituent effect is spread among four bonds in the sp^3 methanes and only among three in the sp^2 ethylenes.

Comparison with Experiment of Predicted Values for $\alpha_H{}^2$

The Δ_X values obtained from $J_{CH}(CH_3X)$, listed in Table II, have been used in Eq. (18) to predict $\alpha_H{}^2$ for eight substituted ethylenes for which J_{CH} has been reported. The results are listed in the middle of Table VI, while in Fig. 5 the corresponding, observed value

TABLE VI. Summary of J_{CH} coupling constants observed in hydrocarbons, with sp^2 and sp hybridization of the carbon orbitals, and "predicted" values[a] for $\alpha_H{}^2$.

Compound	J_{CH} (cps)	$\alpha_H{}^2$	Reference
naphthalene	157	sp^2	b
benzene	159	sp^2	3
mesitylene (2,4,6 protons)	160	sp^2	b
$(CH_3)_2C=C=C^{13}H_2$	166	sp^2	c
cyclohexene	170	sp^2	3
ethylene	157±2	0.336	2
$CHCl=CH_2$ (*cis*)[d]	160	0.341	e
$CHCl=C^{13}H_2$ (*trans*)[d]	161	0.341	e
1,1 dichloroethylene	166	0.349	e
$CH_2=C^{13}HCl$	195	0.402	e
cis$CHCl=CHCl$	198.5	0.408	e
trans$CHCl=CHCl$	199.1	0.408	e
$CCl_2=CHCl$	201.2	0.416	e
$CH_3C\equiv C^{13}-H$	248	sp	2
$\phi C\equiv C^{13}-H$	251	sp	2
$H-C\equiv C-C\equiv C-H$	259.4	sp	c

[a] For those compounds with $\alpha_H{}^2$ listed as sp^2 or sp, there is at present no simple means of correcting for the substituent effects. For the ethylenes, $\alpha_H{}^2$ was obtained with Eq. (18) using Δ_X values from Table II for the methanes.

[b] P. C. Lauterbur, J. Chem. Phys. **26**, 217 (1957).

[c] E. Snyder and J. D. Roberts, J. Am. Chem. Soc. **84**, 1582 (1962).

[d] Cl is *cis* or *trans* to the proton to which C^{13} is coupled.

[e] E. B. Whipple, W. E. Stewart, G. S. Reddy, and J. H. Goldstein, J. Chem. Phys. **34**, 2136 (1961).

for J_{CH} is plotted against the predicted α_H^2. The straight line in the figure corresponds to $J_{CH}=J_0\alpha_H^2=500\alpha_H^2$ cps, and the open circles for the ethylenes should fall on this line if the theory is correct and the *s* electron affinities of substituents are transferrable from aliphatic to olefinic derivatives. It may be seen that the circles are consistently 5 to 10 cps below the theoretical line, suggesting a deficiency in the treatment of the substituted ethylenes.

Some check on the significance of the deviations is afforded by the other points plotted in Fig. 5. Two sets of points represent the J_{CH} values observed for the five sp^2 and the three *sp* hydrocarbons listed in Table VI, with α_H^2 taken to be $\frac{1}{3}$ and $\frac{1}{2}$, respectively. In these cases no corrections have been applied to α_H^2 for the (unknown) substituent effects. The remaining points are for the polysubstituted methanes in Table III, with the α_H^2 values being those predicted for additive substituent effects. These points fall very close to the theoretical line, showing graphically the accuracy of the additivity relation for substituted methanes. In some cases the experimental uncertainties in J_{CH} are comparable with the scatter of points from the line. The points for sp^2 and *sp* compounds, without correction for substituents, exhibit relatively large displacements, both positive and negative, from the line. But the overall scatter of the points is small enough, in spite of the wide range of α_H^2 and J_{CH} covered, to show that the magnitude of the C^{13}–H coupling constant is indeed determined mainly by the *s* character of the C–H bond[19] and that the Fermi contact term is the dominant term in the coupling.

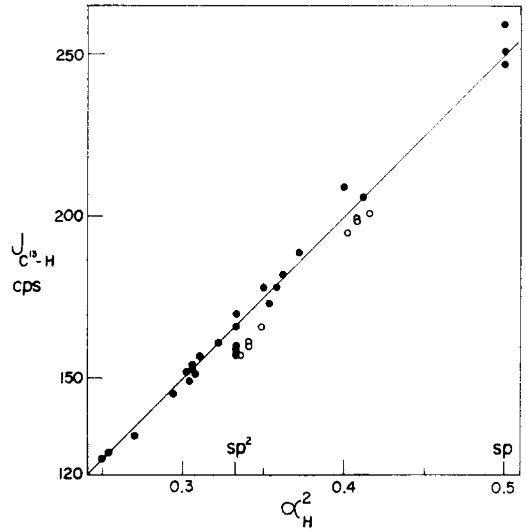

FIG. 5. A plot of observed J_{CH} values versus predicted values of α_H^2. The straight line is $J_{CH}=500\ \alpha_H^2$ cps, upon which all points would fall if the methods for predicting α_H^2 were sufficiently accurate. The points at $\alpha_H^2=\frac{1}{3}$ and $\frac{1}{2}$, i.e., for sp^2 and *sp* hybridization, are from Table VI with no corrections for the effects of substituents upon the hybridization. The open circles are for the substituted ethylenes in Table VI, for which α_H^2 was predicted using the Δ_X values obtained from substituted methanes. The other points represent the polysubstituted methanes in Table III, for which α_H^2 was predicted by the additivity relation.

TABLE VII. Si^{29}–H coupling constants observed in SiH_4 and the silyl halides[a] and the substituent parameters ζ_X obtained from them.

SiH_3X	J_{SiH}(obs)[a] (cps)	ζ_X (cps)
SiH_4	202.5	67.5
SiH_3F	229	94
SiH_3Cl	238.1	103.1
SiH_3Br	240.5	105.5
SiH_3I	240.1	105.1

[a] E. Ebsworth and J. J. Turner, J. Chem. Phys. **36**, 2628 (1962). We wish to thank the authors for making these results available to us prior to publication.

π-Electron Contributions to J_{CH}

Nonetheless, the fact that the circles for the substituted ethylenes fall quite closely along a straight line about 7 cps below the one drawn in Fig. 5, leaves little doubt about there being a real, systematic discrepancy. Part of the discrepancy could result from our assumption of +0.008 for Δ_{CH_2}, which enters in each of the predicted α_H^2 values. However, for this to be the sole factor, Δ_{CH_2} would need to be −0.040 and such a negative value seems an unreasonable departure from the Δ_X values for the methanes. It appears more likely that a π electron contribution to J_{CH} is involved in the ethylenes. This can be estimated by the following extension of Karplus' formulation[20] for the π contribution to J_{HH}, namely—

$$J_{CH}^{\pi}=2.1\times10^{-15}a^{H}a^{C}/\Delta\pi, \qquad (20)$$

where, for ethylene, $\Delta\pi=6$ eV and a^H, the proton hyperfine splitting constant is -65×10^6 cps. The C^{13} hyperfine splitting constant a^C may be estimated by the

TABLE VIII. Deviations (δ) from additivity of the Si–H coupling constants observed[a] in the di- and tri-halosilanes.

SiH_nX_{4-n}	J_{SiH}(obs)[a] (cps)	J_{SiH}(add)[b] (cps)	δ (cps)
SiH_2F_2	282	255.5	26.5
SiH_2Cl_2	288	273.7	14.3
SiH_2Br_2	289	278.5	10.5
SiH_2I_2	280.5	277.7	2.8
$SiHF_3$	381.7	282	99.7
$SiHCl_3$	362.9	309.3	53.6

[a] E. Ebsworth and J. J. Turner, J. Chem. Phys. **36**, 2628 (1962). We wish to thank the authors for making these results available to us prior to publication.
[b] $J_{SiH}(\text{add})=\zeta_X+\zeta_Y+\zeta_Z$, or $(n-1)\zeta_H+(4-n)\zeta_X$ for SiH_nX_{4-n}.

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[19] Also noted previously by Muller and Pritchard,[2] and by Shoolery.[3]

[20] M. Karplus, J. Chem. Phys. **33**, 1842 (1960).

Karplus–Fraenkel expression,[21] which for the $C\dot{C}H_2$ fragment involved here is given by

$$a^{C} = S^{C} + Q_{CC'}{}^{C} + 2Q_{CH}{}^{C}. \qquad (21)$$

Using their values for the parameters, $S^{C} = -12.7$, $Q_{CC'}{}^{C} = +14.4$, and $Q_{CH}{}^{C} = +19.5$, one obtains the result $a^{C} = +40.7$ G.

This leads to a value for $J_{CH}{}^{\pi}$ equal to -2.6 cps, which is of the same sign and order of magnitude as the discrepancy. The agreement provides some indirect evidence that the C^{13} hyperfine interaction constant is positive in free radicals related to ethylenes. Also, it leads us to suggest that at least some of the spread of the sp^2 and sp points in Fig. 5 reflects differences in $J_{CH}{}^{\pi}$, and thus in a^{C}, and that a more detailed study of the matter is desirable.

A final point on the substituted ethylenes is that the various bond angles inferred from the predicted values of $\alpha_H{}^2$ and $\alpha_X{}^2$ do not agree well with experiment. The data available are limited, but it appears that the differences and the factors involved are very similar to those discussed in Sec. II for the methanes.

IV. HALOSILANES SiH_nX_{4-n}

Examination of the data in Tables VII and VIII shows that the Si^{29}–H coupling constants of substituted silanes can be arranged in the same order as their corresponding methane analogs (except for CH_2F_2). This seems to indicate that in the silanes, the J_{SiH} dependence on λ_{Si-H} and s character of the Si–H bond is of the same form as in the methanes. However, as noted previously,[7] and as may be seen in Table VIII for the di- and tri-halo silanes, the substituent effects in the silanes deviate by as much as 30% from the additivity rule followed by the methanes.

Deviations from Additivity of Substituent Effects

The case of the substituted silanes is complicated by the possibility of d hybridization with s and p, which is assumed to be negligible in the case of the methanes owing to the large carbon $2p \rightarrow 3d$ promotional energy required. The promotional energy from $3p$ to $3d$ in Si is much smaller, so that some d character may be expected in the Si hybrid orbitals. This complicates matters because it introduces an additional parameter into the expression for J_{SiH}, and our initial reaction[7] was that the d electrons might be the cause of the deviations from additive substituent effects. But further study of the question indicates that the deviations may result in large part from the greater polarizability of Si, compared to C, and the correspondingly larger changes in λ_{Si-H}.

The deviations δ from additivity for the halosilanes in Table VIII are found to be systematic in the following ways:

(1) They are all positive, that is

$$J_{obs} = J_{add} + \delta,$$

where J_{obs} and J_{add} are taken to be positive.

(2) They occur in the order of the halogens, namely

$$\delta(SiH_2F_2) > \delta(SiH_2Cl_2) > \delta(SiH_2Br_2) > \delta(SiH_2I_2)$$

and

$$\delta(SiHF_3) > \delta(SiHCl_3).$$

(3) For a given halogen, the deviation increases with the number of substituents,

$$\delta(SiHX_3) > \delta(SiH_2X_2).$$

Changes in λ_{Si-H} can account for these three observed trends.

Inductive Changes in λ_{Si-H} and Their Effect upon J_{SiH}

Consider the effect of an electronegative substituent X on λ_{C-H} [the coefficient of the $\phi_C(1)\phi_C(2)$ term] vs that on λ_{Si-H} [the coefficient of the $\phi_H(1)\phi_H(2)$ term], in a wave function such as that defined by Eq. (7). The main differences between the methanes and silanes in this respect are: (a) the direction of change of λ_{M-H} with increasing electronegativity of substituent X and with increasing number of substituents, and (b) the order of magnitude of the change of λ_{M-H}. In both cases the effect is to increase the effective electronegativity X_M of the central atom M insofar as the M–H bond is concerned. We expect the effect of the halogens to be in the order F>Cl>Br>I (electronegativities 4.0>3.0>2.8>2.5) and, of course, $X_3 > X_2 > X$. This leads to an increase in the electronegativity difference $|X_C - X_H|$ for the C–H bond ($X_C > X_H$) and a *decrease in* $|X_{Si} - X_H|$ for the Si–H bond ($X_H > X_{Si}$).

In general, the coefficient λ_{A-B} of the ionic term in the perfect pairing wavefunction describing the bond A–B is related to $|X_A - X_B|$ (e.g., by a relationship such as shown in Fig. 1). Although the exact relationship is disputable, it is known that as $|X_A - X_B|$ increases, so does λ_{A-B}.[22] Thus (a) by the previous discussion, the effect of a more electronegative substituent or a greater number of substituents is toward increasing λ_{C-H} and *decreasing* λ_{Si-H}, and (b) since the polarizability of the electron cloud of Si is much greater than that of C, the effect of the electronegative substituent(s) on the electron distribution in Si is much more drastic than that on C. Therefore, with the same substituent(s), the change in λ_{Si-H} is expected to be of greater magnitude than the change in λ_{C-H}.

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[21] M. Karplus and G. K. Fraenkel, J. Chem. Phys. **35**, 1312 (1961).

[22] See for example: L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, New York, 1960), p. 99; B. P. Dailey and C. H. Townes, J. Chem. Phys. **23**, 118 (1955); W. Gordy, *ibid.* **19**, 792 (1951).

The form of $J_{\rm SiH}$ under approximations similar to those used in deriving Eqs. (10) and (11) for the methanes, is[23]

$$J_{\rm SiH}=\frac{\gamma_{\rm Si}\gamma_{\rm H}}{h\Delta E}\left(\frac{16\pi\beta\hbar}{3}\right)^2\eta^2\alpha^2\,|\,3s_{\rm Si}(0)\,|^2\,|\,1s_{\rm H}(0)\,|^2, \qquad (22)$$

where

$$\eta^{-2}=[2+2(\alpha^2S_s^2+\beta^2S_p^2+\gamma^2S_d^2)+4(\alpha\beta S_sS_p+\beta\gamma S_pS_d+\alpha\gamma S_sS_d)+4\lambda_{\rm Si-H}(\alpha S_s+\beta S_p+\gamma S_d)+\lambda_{\rm Si-H}^2]. \qquad (23)$$

In Eq. (23) α^2, β^2, and γ^2 are, respectively, the s, p, and d character of the Si hybrid orbital for the Si-H bond, and S_s, S_p, and S_d are the overlap integrals between the 1s orbital on H and the respective orbitals on Si.

With the use of Eq. (22), the expression for the deviation from additivity,

$$\delta=|\,J_{\rm obs}({\rm SiH}_n{\rm X}_{4-n})\,|-|\,J_{\rm add}\,|,$$

may be written as

$$\delta=|\,A\,|\,[\eta^2({\rm SiH}_n{\rm X}_{4-n})-\eta^2({\rm SiH}_4)]\alpha^2, \qquad (24)$$

where A is a collection of constants. From Eq. (23) we see that a decrease in $\lambda_{\rm Si-H}$ leads to a larger η^2. Therefore, the decrease in $\lambda_{\rm Si-H}$ produced by replacement of a hydrogen with a substituent which is more electronegative than hydrogen, causes $\eta^2({\rm SiH}_n{\rm X}_{4-n})$ to be *greater* than $\eta^2({\rm SiH}_4)$. Hence, the deviations δ are all positive. Furthermore, since by the previous discussion the effect on $\lambda_{\rm Si-H}$ is more drastic as one goes from X=I to X=F and from SiH_3X to $SiHX_3$, then the deviations should be in the order, as observed

$$\delta({\rm SiH_2F_2})>\delta({\rm SiH_2Cl_2})>\delta({\rm SiH_2Br_2})>(\delta({\rm SiH_2I_2})$$

$$\delta({\rm SiHF_3})>\delta({\rm SiHCl_3}),$$

and

$$\delta({\rm SiHX_3})>\delta({\rm SiH_2X_2}).$$

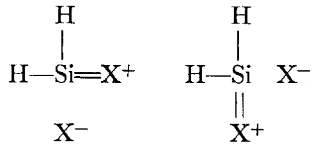
Therefore, it seems that the deviations of $J_{\rm SiH}$ from additivity are governed by the inductive effect of the electronegative substituents.

Discussion

Such inductive effects should also occur in the silyl halides, but the evidence on this point is obscure. For the methanes, the $\Delta_{\rm X}$ values are about +0.20 for all four halogens. However, for the silanes, the "apparent" $\Delta_{\rm X}$ increases from +0.13 for F to +0.19 for Br and I. This trend is the reverse of what would be predicted on the basis of the proposed inductive effects, if the $\Delta_{\rm X}$ values would otherwise be about the same for silanes and methanes. The close agreement between the Br and I $\Delta_{\rm X}$ values for methanes and silanes (+0.20 and +0.19) suggests that further comparisons of this sort may be significant. In fact, the deviations from additivity in the halomethanes, although small, parallel[24] the deviations in the halosilanes, i.e., $\delta({\rm CHX_3})>\delta({\rm CH_2X_2})$ and in the order F>Cl>Br>I (+12, +3, −1, −4, respectively, for CH_2X_2). But this does not necessarily mean that the factor(s) responsible for the deviations in the halosilanes is the same factor which causes the small deviations in the halomethanes. The latter are in the wrong direction to be explained by the inductive effect on $\lambda_{\rm C-H}$ although the deviations in the silanes are compatible with changes in $\lambda_{\rm Si-H}$.

An accurate theoretical estimate of the inductive effects upon $J_{\rm SiH}$ would require at least a knowledge of all the appropriate constants in Eqs. (22) and (23). However, several of these are not available so a simplified treatment was made by neglecting the d electron terms in Eq. (23) for η^2, calculating the remaining overlap integrals,[11] and obtaining an equation for $\eta^2(\lambda_{\rm Si-H}, \alpha^2)$. Reference to Fig. (1) indicates that $\lambda_{\rm Si-H}({\rm SiH_4})$ is about 0.35. With this value, and the equation for η^2, it was found that $\lambda_{\rm Si-H}$ would need to be 0.23 in SiH_2F_2 if $\delta({\rm SiH_2F_2})$ were entirely due to the inductive effect. Such a change, while large, is not unreasonable.

We have not considered the complication of the silane problem by the reasonance effect, i.e., contributions by structures of the form



$$\overset{\rm H}{\rm H{-}Si{=}X^+}\ \ {\rm X^-} \qquad \overset{\rm H}{\rm H{-}\underset{X^+}{Si}}\ \ {\rm X^-}.$$

These are expected to be greatest for F and least for I, for it is well known that large atoms form multiple bonds less readily. This effect is probably also present in the methanes but to a smaller extent, for Si can form $d\pi$ bonds. This resonance effect tends to make Si more electropositive, which is opposite to the inductive effect. In addition, the above structures bring up the possibility of π contributions to the Si-H coupling. In view of the consistent trend in the deviations δ it seems that these two effects largely cancel one another, thus maintaining the trends in δ which would be expected from inductive effects alone.

In the foregoing discussions we have ignored altogether the noncontact contributions (O_1 and O_2). Karplus and Grant[1] estimated O_1 and O_2 to be 2 and 8 cps, respectively, for CH_4 and stated that these contributions are not necessarily small for compounds which deviate from tetrahedral symmetry. The contributions O_1 and O_2 are extremely difficult to calculate at present, but an approximate relationship has been found by

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[23] This is not to say that the same approximations are good for the silanes. We present this equation to illustrate the dependence of $J_{\rm SiH}$ on $\lambda_{\rm Si-H}$. Note that $\gamma_{\rm Si}$ is a negative quantity.

[24] We wish to thank a referee for calling this relation to our attention.

Pople[25] between $O_{1NN'}$ and the anisotropy of the screening constants for N and N'. An extension of this treatment to $O_{1\mathrm{CH}}$ and $O_{1\mathrm{SiH}}$ shows that these contributions to J_{CH} and $J_{\mathrm{Si-H}}$ are not additive.

As a final point, the deviations from additivity indicate that such factors as inductive effect on λ, contributions of doubly-bonded ionic structures to the ground state, and noncontact terms may very well be responsible for some part of the substituent parameter ζ_{X} which we have treated here as if it were attributable entirely to hybridization changes.

APPENDIX

In the derivation of Eq. (8) the following, usual approximation was used:

$$\langle\phi_N(\mathbf{r}_1)\mid\delta(\mathbf{r}_{1N''})\mid\phi_{N'}(\mathbf{r}_1)\rangle\cong|\phi_N(0)|^2\delta_{NN''}\delta_{N'N''},\tag{25}$$

where $\phi_N(\mathbf{r}_1)$ is an atomic orbital centered on nucleus N. For N and N' separated by two or more bonds, this is a very good approximation which has always been used in calculating $J_{NN'}$, as in the case of H—C—C—H′. In order to determine how valid this approximation is in the case of directly bonded nuclei,[26] more specifically for J_{CH}, let us examine in detail the integral involved in deriving Eq. (8), namely

$$\rho=\tfrac{1}{2}\langle u(1,2)\mid\delta(\mathbf{r}_{1\mathrm{H}})\delta(\mathbf{r}_{2\mathrm{C}})+\delta(\mathbf{r}_{2\mathrm{H}})\delta(\mathbf{r}_{1\mathrm{C}})\mid u(1,2)\rangle+\rho_{\mathrm{B}}\tag{26}$$

where

$$\rho_{\mathrm{B}}=\tfrac{1}{2}\sum_{B=X,Y,Z}\langle u_{\mathrm{B}}(1,2)\mid\delta(\mathbf{r}_{1\mathrm{H}})\delta(\mathbf{r}_{2\mathrm{C}})+\delta(\mathbf{r}_{2\mathrm{H}})\delta(\mathbf{r}_{1\mathrm{C}})\mid u_{\mathrm{B}}(1,2)\rangle,\tag{27}$$

with

$$u_{\mathrm{H}}(1,2)=\eta[\phi_{\mathrm{H}}(1)\phi_{\mathrm{C}}(2)+\phi_{\mathrm{C}}(1)\phi_{\mathrm{H}}(2)+\lambda_{\mathrm{H}}\phi_{\mathrm{H}}(1)\phi_{\mathrm{H}}(2)+\lambda_{\mathrm{C}}\phi_{\mathrm{C}}(1)\phi_{\mathrm{C}}(2)],$$

and

$$u_{\mathrm{X}}(1,2)=\eta_{\mathrm{X}}[\phi_{\mathrm{X}}(1)\phi_{\mathrm{C}}'(2)+\phi_{\mathrm{C}}'(1)\phi_{\mathrm{X}}(2)+\lambda_{\mathrm{X}}\phi_{\mathrm{X}}(1)\phi_{\mathrm{X}}(2)+\lambda_{\mathrm{C}}'\phi_{\mathrm{C}}'(1)\phi_{\mathrm{C}}'(2)],$$

in which ϕ_{C} is the carbon hybrid orbital directed toward the hydrogen and $\phi_{\mathrm{C}'}$ is the carbon hybrid orbital directed toward the substituent X. The leading term which arises upon calculating the integral ρ is

$$\rho_0=\eta^2|\phi_{\mathrm{C}}(0)|^2|\phi_{\mathrm{H}}(0)|^2=\eta^2\alpha_{\mathrm{H}}^2|2s_{\mathrm{C}}(0)|^2|1s_{\mathrm{H}}(0)|^2.$$

The use of the approximation expressed in Eq. (25) in evaluating ρ gives rise to only the leading term, and this results in Eq. (10). The other, smaller terms in ρ are products of integrals of the form,

$$\langle\phi_{\mathrm{H}}(\mathbf{r}_i)\mid\delta(\mathbf{r}_{i\mathrm{H}})\mid\phi_{\mathrm{H}}(\mathbf{r}_i)\rangle=\phi_{\mathrm{H}}(0)\phi_{\mathrm{C}}(R),$$

where R is the equilibrium distance between the C and H nuclei.

The complete expression for ρ is given by

$$\begin{aligned}\rho/\eta^2=&\,|\phi_{\mathrm{H}}(0)|^2|\phi_{\mathrm{C}}(0)|^2+|\phi_{\mathrm{H}}(R)|^2|\phi_{\mathrm{C}}(R)|^2\\&+\lambda_{\mathrm{H}}^2|\phi_{\mathrm{H}}(0)|^2|\phi_{\mathrm{H}}(R)|^2+\lambda_{\mathrm{C}}^2|\phi_{\mathrm{C}}(0)|^2|\phi_{\mathrm{C}}(R)|^2\\&+2(1+\lambda_{\mathrm{C}}\lambda_{\mathrm{H}})[\phi_{\mathrm{H}}(0)\phi_{\mathrm{C}}(R)\phi_{\mathrm{C}}(0)\phi_{\mathrm{H}}(R)]\\&+2\lambda_{\mathrm{H}}[|\phi_{\mathrm{H}}(0)|^2\phi_{\mathrm{C}}(0)\phi_{\mathrm{H}}(R)+|\phi_{\mathrm{H}}(R)|^2\phi_{\mathrm{C}}(R)\phi_{\mathrm{H}}(0)]\\&+2\lambda_{\mathrm{C}}[|\phi_{\mathrm{C}}(0)|^2\phi_{\mathrm{H}}(0)\phi_{\mathrm{C}}(R)+|\phi_{\mathrm{C}}(R)|^2\phi_{\mathrm{H}}(R)\phi_{\mathrm{C}}(0)]\\&+\rho_{\mathrm{B}}/\eta^2.\end{aligned}$$

The terms in the summation, Eq. (27), which contribute the most to ρ_{B} are of the form

$$4\eta_{\mathrm{X}}^2\langle\phi_{\mathrm{C}'}(1)\mid\delta(\mathbf{r}_{1\mathrm{C}})\mid\phi_{\mathrm{C}'}(1)\rangle\langle\phi_{\mathrm{X}}(2)\mid\delta(\mathbf{r}_{2\mathrm{H}})\mid\phi_{\mathrm{X}}(2)\rangle$$

and

$$2\eta_{\mathrm{X}}^2\lambda_{\mathrm{CX}}^2\langle\phi_{\mathrm{C}'}(1)\mid\delta(\mathbf{r}_{1\mathrm{C}})\mid\phi_{\mathrm{C}'}(1)\rangle\langle\phi_{\mathrm{C}'}(2)\mid\delta(\mathbf{r}_{2\mathrm{H}})\times\mid\phi_{\mathrm{C}'}(2)\rangle.$$

$\langle\phi_{\mathrm{X}}(2)\mid\delta(\mathbf{r}_{2\mathrm{H}})\mid\phi_{\mathrm{X}}(2)\rangle$ is the density at the H nucleus of an electron in the X orbital, which is vanishingly small, and $\langle\phi_{\mathrm{C}}'(2)\mid\delta(\mathbf{r}_{2\mathrm{H}})\mid\phi_{\mathrm{C}}'(2)\rangle$ is the density at the H nucleus of an electron in the carbon hybrid orbital directed toward X, which is also small and approximately equal to $\alpha_{\mathrm{X}}^2|s_{\mathrm{C}}(R)|^2$. Therefore ρ_{B}, the contribution to ρ of the orbitals involved in the other bonds, clearly is very small.

The hydrogen atom 1s wavefunction gives $\phi_{\mathrm{H}}(0)=0.5642$ and $\phi_{\mathrm{H}}(R)=0.0716$ in units of $a_0^{\frac{3}{2}}$; and from the Hartree–Fock atomic wavefunctions for carbon we obtain the values

$$2s_{\mathrm{C}}(0)=1.664\qquad 2s_{\mathrm{C}}(R)=-0.0791$$
$$2p_\sigma(0)=0\qquad 2p_\sigma(R)=0.0788,$$

which lead to

$$\phi_{\mathrm{C}}(0)=1.664\alpha_{\mathrm{H}}$$
$$\phi_{\mathrm{C}}(R)=-0.0791\alpha_{\mathrm{H}}+0.0788(1-\alpha_{\mathrm{H}}^2)^{\frac{1}{2}}.$$

The range of α_{H}^2 of interest here is 0.25 to 0.50. $\phi_{\mathrm{C}}(R)$ is equal to 0.0287 for $\alpha_{\mathrm{H}}^2=0.25$ and decreases monotonically and reaches zero at $\alpha_{\mathrm{H}}^2=0.498$. ρ_{B} also decreases monotonically with increasing α_{H}^2. Therefore, by using the value of $\phi_{\mathrm{C}}(R)$ for $\alpha_{\mathrm{H}}^2=0.25$, one can find the upper limit for the error incurred by dropping all terms containing $\phi_N(R)$; i.e., in using the approximation expressed by Eq. (25).

Using $\lambda_{\mathrm{C}}=0.374$ and $\lambda_{\mathrm{H}}=0.01$, one obtains $\rho_0/\eta^2=0.2203$ and $\rho/\eta^2=0.2312+\rho_{\mathrm{B}}/\eta^2$ in units of a_0^6. ρ_{B}/η^2 is found to be 0.0005 in CH_4. The maximum error is, therefore, 5% or 6 cps. The percentage error decreases monotonically with α_{H}^2 and goes to a minimum of 0.17% at $\alpha_{\mathrm{H}}^2=0.498$, where J_{CH} is around 250 cps, i.e., an error of 0.4 cps.

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[25] J. A. Pople, Mol. Phys. **1**, 216 (1958).

[26] We wish to thank Dr. Ralph M. Deal for raising the question which led to this analysis.