the metal concentration, and since the equation[5] used involves the refractive index of the solid salt and complex polarizability of the electron in a solid, we can only estimate that the oscillator strength is less for the molten system than for the solid. This can be interpreted as indicating an interaction of the electron with the ions surrounding it.

(5) F. Seitz, "Modern Theory of Solids," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 665.

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Proton–^{13}C Spin–Spin Coupling. V. Inadequacy of Correlation of Proton–^{13}C Coupling with s-Character

Sir:

The short-range proton-^{13}C coupling, $J_{^{13}CH}$, has been extensively investigated.[1] The general linearity between $J_{^{13}CH}$ and fractional s-character of the ^{13}C hybrid atomic orbital has led to the conclusion that the contact term is essentially the sole contributor to the coupling. Additivity relations, with some exceptions,[1e] of substituent effects on $J_{^{13}CH}$ in substituted methanes[1f] and formyl compounds[1g] have been discovered. For the former compounds this additivity has been derived and interpreted from valence bond theory.[1h] On the assumption therefore that the contact term is essentially the sole contributor to the coupling, fractional s-characters have been calculated, usually in three significant figures, from experimental $J_{^{13}CH}$ values.

Long-range proton-^{13}C coupling has enjoyed less attention than $J_{^{13}CH}$. From the approximate linearity between $J_{^{13}CCH}$ and fractional s-character of the ^{13}C hybrid atomic orbital, it was concluded[2] that the contact term dominates this coupling when the ^{13}CCH angle is tetrahedral. No such obvious correlation was found[3] in $J_{^{13}CCCH}$.

We shall present data that focus attention on the inadequacy of correlation of proton–^{13}C coupling with s-character.

Three-Bond Coupling.—Table I summarizes $J_{^{13}CCCH}$ values, accurate to ± 0.05 c.p.s., for a few selected $(CH_3)_3C^{13}C$ compounds. The failure of a single factor[4] to accommodate the data is obvious. The most striking and pertinent observations are: unusually high values for the halogen compounds; increase of these values in the order chloro < bromo < iodo, whereas from halogen electronegativities the reverse order is expected (see *para*-substituted neopentyl benzoates and phenyl pivalates); and greater variation of the values for the halogen compounds when the ^{13}C is sp^2 rather than sp^3 hybridized. These results could be interpreted in terms of spin-dipole and/or electron-orbital contributions to the coupling (interactions between the proton magnetic moment and currents induced on the halogen by the ^{13}C nucleus), since such contributions should be significant when the substituent has anglular-dependent atomic orbitals (p, d, f); and increase in the order chloro < bromo < iodo.

TABLE I

$J_{^{13}CCCH}$ of $(CH_3)_3C^{13}C$ Compounds

Compound	$J_{^{13}CCCH}$
$(CH_3)_3C^{13}CH_2OH$	4.48
$(CH_3)_3C^{13}CH_2OCOC_6H_4OCH_3(p)$	4.74
$(CH_3)_3C^{13}CH_2OCOC_6H_5$	4.81
$(CH_3)_3C^{13}CH_2OCOC_6H_4NO_2(p)$	4.91
$(CH_3)_3C^{13}CH_2Cl$	5.63
$(CH_3)_3C^{13}CH_2Br$	5.84
$(CH_3)_3C^{13}CH_2I$	5.99
$(CH_3)_3C^{13}C(CH_3){=}CH_2$	4.00
$(CH_3)_3C^{13}C(CH_3){=}O$	4.20
$(CH_3)_3C^{13}CO_2H$	4.38
$(CH_3)_3C^{13}CO_2C_6H_4OCH_3(p)$	4.58
$(CH_3)_3C^{13}CO_2C_6H_5$	4.60
$(CH_3)_3C^{13}CO_2C_6H_4NO_2(p)$	4.76
$(CH_3)_3C^{13}COCl$	5.99
$(CH_3)_3C^{13}COBr$	6.43
$(CH_3)_3C^{13}C{\equiv}N$	5.38

Two-Bond Coupling.—The magnitude of $J_{^{13}CCH}$ for acetyl halides (Table II) is also consistent with possible spin-dipole and/or electron-orbital contributions to the two-bond coupling.

TABLE II

$J_{^{13}CCH}$ of CH_3–^{13}C Compounds

Compound	$J_{^{13}CCH}$	Compound	$J_{^{13}CCH}$
$CH_3{}^{13}C[(CH_3)_3C]{=}CH_2$	6.40	$CH_3{}^{13}CO_2C_6H_4NO_2(p)$	7.16
$(CH_3)_2{}^{13}C{=}O$	5.90	$CH_3{}^{13}CONH_2$	6.01
$CH_3{}^{13}CO_2H$	6.80	$CH_3{}^{13}COCl$	7.58
$CH_3{}^{13}CO_2C_6H_4OCH_3(p)$	7.00	$CH_3{}^{13}COBr$	7.60
$CH_3{}^{13}CO_2C_6H_5$	7.04	$CH_3{}^{13}COI$	7.30

One-Bond Coupling.—If the spin-dipole and/or electron-orbital terms contribute to long-range proton-^{13}C coupling, it is only reasonable to expect that they may contribute to $J_{^{13}CH}$. The following could be interpreted in such terms. (a) Increase in the electronegativity of the group attached to the ^{13}C should increase $J_{^{13}CH}$; *e.g.*, for neopentyl-1-^{13}C benzoates as the *para* substituent changes from methoxy to hydrogen to nitro, $J_{^{13}CH}$ changes from 145.7 to 146.1 to 146.8 c.p.s., yet for the neopentyl-1-^{13}C halides $J_{^{13}CH}$ changes from 147.9 (chloro) to 149.1 (bromo) to 148.0 c.p.s. (iodo). Methyl halides show the same trend[1]: 150 (chloro), 152 (bromo), 151 c.p.s. (iodo).[5] (b) If the ^{13}C is sp^2 hybridized, $J_{^{13}CH}$ values are unusually high when a halogen or oxygen is bonded to it; *e.g.*, for formyl fluoride[1d] and methyl formate,[1d] $J_{^{13}CH}$ values are 267 and 226 c.p.s. respectively. That the effect may be detectable even when the halogen is not directly bonded to the ^{13}C is shown by the higher $J_{^{13}CH}$ values of *ortho*-substituted benzaldehydes when the *ortho* substituent is a group with angular-dependent atomic orbitals; *e.g.*, $J_{^{13}CH}$ (c.p.s.) = 174 (benzaldehyde), 173.5 (2-methyl), 174 (3-methyl), 173.5 (4-

(1) (a) P. C. Lauterbur, *J. Chem. Phys.*, **26**, 217 (1957); *J. Am. Chem. Soc.*, **83**, 1838, 1846 (1961); (b) J. N. Shoolery, *J. Chem. Phys.*, **31**, 1427 (1959); (c) N. Muller and D. E. Pritchard, *ibid.*, **31**, 768, 1471 (1959); (d) N. Muller, *ibid.*, **36**, 359 (1962); (e) N. Muller and P. I. Rose, *J. Am. Chem. Soc.*, **84**, 3973 (1962); (f) E. R. Malinowski, *ibid.*, **83**, 4479 (1961); (g) E. R. Malinowski, L. Z. Pollara, and J. P. Larmann, *ibid.*, **84**, 2649 (1962); (h) H. S. Gutowsky and C. S. Juan, *ibid.*, **84**, 307 (1962); *J. Chem. Phys.*, **37**, 2198 (1962); (j) H. Dreeskamp and E. Sackmann, *Z. Physik. Chem.*, (Frankfurt), **34**, 273 (1962).

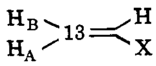
(2) G. J. Karabatsos, J. D. Graham, and F. M. Vane, *J. Phys. Chem.*, **65**, 1657 (1961).

(3) G. J. Karabatsos, J. D. Graham, and F. M. Vane, *J. Am. Chem. Soc.*, **83**, 2778 (1961); *ibid.*, **84**, 37 (1962).

(4) Detailed discussion of each contributing factor, *e.g.*, substituent electronegativity, angle deformations, hybridization, etc., will be given later.

(5) This anomaly has been interpreted previously (ref. 1c) in terms of increases in ρ_{C-H} as the C–X interatomic distance increases.

methyl), 182 (2-fluoro), 178 (3-fluoro), 175.5 (4-fluoro), 182.5 (2-bromo), 177.5 (3-bromo), 180 (2-methoxyl), 175.5 (3-methoxy), and 173 (4-methoxy). (c) In system I, when X = C_6H_5, $J_{^{13}CH_A}$ = 156 and $J_{^{13}CH_B}$ = 162 c.p.s.; when X = Cl, $J_{^{13}CH_A}$ = 160 and $J_{^{13}CH_B}$ =



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161 c.p.s.[6] When X = Br, $J_{^{13}CH_A}$ = 163.8 and $J_{^{13}CH_B}$ = 159.6 c.p.s.[7] This change in the $J_{^{13}CH_A}/J_{^{13}CH_B}$ ratio from styrene to vinyl bromide is also consistent with contributions from the spin-dipole and/or electron-orbital terms.[8]

On the basis of these arguments, it is evident that s-characters calculated from $J_{^{13}CH}$ are unreliable and misleading. Values calculated from the long-range coupling are meaningless even when expressed in one significant figure; those calculated from the short-range coupling are probably equally meaningless whenever two or more heteroatoms are bonded to the ^{13}C.

Acknowledgment.—We thank the United States Atomic Energy Commission for financial support (Grant CCO-1189-11).

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

(7) R. M. Lynden-Bell, *Mol. Phys.*, **6**, 537 (1963).

(8) The validity of our suggestion that spin-dipole and electron-orbital terms contribute to proton-^{13}C coupling certainly requires further experimental scrutiny, in view of theoretical predictions by J. A. Pople, *ibid.*, **1**, 216 (1958) that "coupling *via* currents induced on a third atom will always be negligible."

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Substituent Effects. III.[1] Correlation of ^{13}C–F and ^{29}Si–H Couplings by Pairwise Interactions

Sir:

A "direct" additivity rule for J_{CH} for substituted methanes of the type CHXYZ was first observed by Malinowski[2]; namely, $J_{CH} = \zeta_x + \zeta_y + \zeta_z$, where ζ_x is a parameter associated with substituent x. Significant departures from this simple additivity rule have been reported[3–5] for compounds which contain highly electronegative substituents. Recently, Douglas[6] introduced pairwise interaction terms as corrections for departures from "direct" additivity. Essentially, his equation can be written as $J_{CH} = \zeta_x + \zeta_y + \zeta_z + \zeta_{xy} + \zeta_{xz} + \zeta_{yz}$, where ζ_{xy} is an interaction parameter associated with substituents x and y, and is independent of substituent z.

Recently it has been reported that J_{CF}[3,7] and J_{SiH}[8,9] do not obey the "direct" additivity rule. We wish to report here that J_{CF} and J_{SiH} can be correlated by pairwise interactions. For simplicity, we will redefine the interaction parameter by $\eta_{xy} = \zeta_{xy} + 0.5(\zeta_x + \zeta_y)$, so that the equation above becomes $J(xyz) = \eta_{xy} + \eta_{xz} + \eta_{yz}$, where J(xyz) is a coupling constant for a compound containing substituents x, y, and z. The parameters shown in Tables I and II have been evaluated in a straightforward manner; namely, $\eta_{xx} = J(xxx)/3$ and $\eta_{xy} = [J(xxy) - \eta_{xx}]/2$, respectively.

TABLE I

INTERACTION PARAMETERS, η_{xx}, FOR J_{CF} AND J_{SiH}, CALCULATED BY $\eta_{xx} = J(xxx)/3$

Interaction parameter	^{13}C–F couplings, c.p.s.	^{29}Si–H couplings,[d] c.p.s.
H,H	52.6[a]	67.5
F,F	86.0[a]	127.2
Cl,Cl	112.2[b]	121.0
Br,Br	124.0[c]	107.9

[a] Calculated from an average of values found by N. Muller and D. J. Carr, *J. Phys. Chem.*, **67**, 112 (1963), and in ref. 5. [b] Calculated from an average of values found by Muller and Carr[a] and in ref. 7. [c] Calculated from an average of values found by R. K. Harris, *J. Mol. Spectry.*, **10**, 309 (1963), and by P. C. Lauterbur in "Determinations of Organic Structures by Physical Methods," Vol. 2, edited by F. C. Nachod and W. D. Phillips, Academic Press, Inc., New York, N. Y., 1962, p. 505. [d] Data taken from ref. 8.

TABLE II

INTERACTION PARAMETERS, η_{xy}, FOR J_{CF} AND J_{SiH}, CALCULATED BY $\eta_{xy} = [J(xxy) - \eta_{xx}]/2$

Interaction parameters	^{13}C–F couplings, c.p.s.	^{29}Si–H couplings,[e] c.p.s.
Cl,H	90.8[a]	83.5
F,H	93.6[b]	77.4
F,Br	119.0[c]	
F,Cl	106.5[c]	
F,CN	89.0[d]	
H,CN	59.7[d]	

[a] Data taken from G. V. D. Tiers, *J. Am. Chem. Soc.*, **84**, 3972 (1962). [b] Calculated from an average of values found by Muller and Carr, footnote *a*, Table I, and in ref. 5. [c] Data taken from Muller and Carr, footnote *a*, Table I. [d] Data taken from ref. 3. [e] Data taken from ref. 8.

A comparison between observed and predicted coupling constants is shown in Table III. Considering that the evaluation of the interaction parameters does not take into account the inherent error in the measured coupling constants, we conclude that the agreement between experiment and prediction is very good. Obviously a trial-and-error or a least-squares

TABLE III

COMPARISON BETWEEN CALCULATED AND OBSERVED COUPLING CONSTANTS

Compound	J_{calcd}, c.p.s.		J_{obsd}, c.p.s.	Difference calcd. − obsd., c.p.s.
	J_{Si-H}			
SiH_3Cl	$\eta_{H,H} + 2\eta_{Cl,H}$	= 234.5	238.1[a]	+3.6
SiH_3F	$\eta_{H,H} + 2\eta_{F,H}$	= 222.3	229.0[a]	+6.7
	J_{C-F}			
CH_2F_2	$\eta_{H,H} + 2\eta_{H,F}$	= 239.7	233.4[b]	+6.3
CF_2Br_2	$\eta_{Br,Br} + 2\eta_{F,Br}$	= 362.0	357.8[c]	+4.2
CF_2Cl_2	$\eta_{Cl,Cl} + 2\eta_{F,Cl}$	= 325.2	324.7[d]	+0.5
CF_2HCN	$\eta_{H,F} + \eta_{H,CN} + \eta_{F,CN}$	= 242.3	243.5[e]	−1.2

[a] Data taken from ref. 8. [b] An average of values found by Muller and Carr, footnote *a*, Table I, and in ref. 5. [c] An average of value found by Muller and Carr,[b] and by Harris, footnote *c*, Table I. [d] An average of values found by Muller and Carr,[b] and by Lauterbur, footnote *c*, Table I. [e] Data taken from ref. 3.

(1) Part II: E. R. Malinowski, L. Z. Pollara, and J. P. Larmann, *J. Am. Chem. Soc.*, **84**, 2649 (1962).

(2) E. R. Malinowski, *ibid.*, **83**, 4479 (1961).

(3) G. P. van der Kelen and Z. Eeckhaut, *J. Mol. Spectry.*, **10**, 141 (1963).

(4) N. Muller and P. I. Rose, *J. Am. Chem. Soc.*, **84**, 3973 (1962).

(5) S. G. Frankiss, *J. Phys. Chem.*, **67**, 752 (1963).

(6) A. W. Douglas, *J. Chem. Phys.*, **40**, 2413 (1964).

(7) R. K. Harris, *J. Phys. Chem.*, **66**, 768 (1962).

(8) E. A. V. Ebsworth and J. J. Turner, *J. Chem. Phys.*, **36**, 2628 (1962).

(9) H. S. Gutowsky and C. S. Juan, *ibid.*, **37**, 2198 (1962).