

pale yellow in color. Dodecamethylcyclohexasilane can be converted to its anion radical in the presence of an excess of benzene, which indicates that the cyclo-silane has a higher electron affinity than benzene.

Preliminary attempts have been made to form anion radicals from other permethylated polysilanes. Hexamethyldisilane gave no radical signal after repeated attempts at reduction, but linear decamethyltetrasilane gave complex e.s.r. spectra under the conditions described above. Attempts to rationalize these spectra are under way, and extensions to related organometallic systems are planned.

G. Ronald Husk, Robert West

Department of Chemistry, University of Wisconsin
Madison, Wisconsin

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The Dependence of Directly Bonded Coupling Constants upon the Effective Nuclear Charge

Sir:

The practice of relating directly bonded carbon-13 proton coupling constants with per cent "s" character in the C-H bond is receiving such general acceptance that a critical evaluation is needed of other factors important in this experimental parameter. The hybridization criterion is based on theoretical considerations^{1,2} and on observed empirical relationships.³⁻⁵ Additive substituent effects⁶ upon ${}^{(1)}J_{\text{C}_{13}\text{-H}}$ have been attributed⁷ also to variations in the bond hybridization.

The importance of factors other than the "s" character of a C-H bond is portrayed in eq. 1, which is

$${}^{(1)}J(K) \cong \left(\frac{\Delta_{\text{CH}_4}}{\Delta_K}\right) \left(\frac{N_K}{N_{\text{CH}_4}}\right)^2 \left(\frac{\alpha_K}{\alpha_{\text{CH}_4}}\right)^2 \left(\frac{Z_K}{Z_{\text{CH}_4}}\right)^3 {}^{(1)}J(\text{CH}_4) \quad (1)$$

obtained directly from eq. 4 of Karplus and Grant,¹ where ${}^{(1)}J(K)$ is the coupling constant in the Kth bond of a substituted methane, ${}^{(1)}J(\text{CH}_4)$ is 125 c.p.s., Δ is the average excitation energy which should not vary greatly for various C-H bonds, N is the bond normalization constant defined previously,¹ α^2 is a parameter which is directly proportional to the "s" character, and Z represents the effective nuclear charge appearing in the radial function of a carbon 2s orbital of the form $(Z_K/a_0)^{3/2}\{A + B(Z_K/a_0)r\} \exp(Z_K r/2a_0)$. It is apparent from eq. 1 that neglect of minor changes in Z , which is raised to the third power as also noted by Shoolery,³ will invalidate conclusions regarding bond hybridization.

As a means of estimating variations in Z_K , it is useful to consider the charge transfer, Q_K , defined by eq. 2

$$Q_K = \frac{2\lambda_K S_K + \lambda_K^2}{2 + 2S_K^2 + 4\lambda_K S_K + \lambda_K^2} \quad (2)$$

for the $u_K(i,j)$ bond orbital (see ref. 1), where the bond overlap is S_K , and λ_K is the corresponding ionic coefficient. Q_K is positive for an electron shift toward the

carbon atom. Application of Slater screening concepts in eq. 3 relates Z_K to Q_K . The summation is over

$$Z_K = Z_0 - S \sum_K' Q_K \quad (3)$$

all bonds centered on the carbon-13 except the C-H bond giving rise to the spin-spin splitting. S is the Slater screening parameter (0.35) and Z_0 is a reference bond effective nuclear charge. Coulson⁸ has suggested that $Z_{\text{CH}_4} = 3.25\beta$ where $\beta = 1.1-1.2$. Using $\beta = 1.15$, it was found that the value of Q_{CH} which gave the best fit for all of the experimental data in Table I was 0.18,⁹ and a value of 3.929 was obtained for Z_0 . The normalization constant, N_K , follows directly from λ_K and S_K , which are specified by eq. 2.

Table I

Compound	$(N_K/N_{\text{CH}_4})^2$	$(Z_K/Z_{\text{CH}_4})^3$	${}^{(1)}J_{\text{CH}}$, c.p.s.		Difference
			Calcd.	Exptl.	
CH ₄	1	1	[125]	125 ^a	0
CH ₃ F	1.033	1.213	156.7	149 ^a	7.7
CH ₃ Cl	1.028	1.181	151.8	151 ^d	0.8
CH ₃ Br	1.025	1.166	149.4	151.0 ^e	-1.6
CH ₃ I	1.021	1.141	145.6	150.5 ^e	-4.9
CH ₃ -O-	1.021	1.138	145.2	140-147 ^f	-1.8 to +5.2
CH ₂ F ₂	1.070	1.454	194.5	185 ^h	9.5
CH ₂ Cl ₂	1.060	1.383	183.3	178 ^a	5.3
CH ₂ ClBr	1.057	1.366	180.5	179.5 ^e	1.0
CH ₂ Br ₂	1.055	1.349	177.8	178 ^e	-0.2
CH ₂ I ₂	1.046	1.294	169.3	173 ^a	-3.7
CH ₂ (OCH ₃) ₂	1.045	1.288	168.3	162 ^b	6.3
CHF ₃	1.106	1.725	238.5	238 ^b	0.5
CHF ₂ Cl	1.101	1.685	231.9	231 ^b	0.9
CHCl ₂ F	1.096	1.646	225.5	220 ^b	5.5
CHCl ₃	1.091	1.607	219.1	209 ^a	10.1
CHBr ₃	1.084	1.550	209.9	206 ^a	3.9
CHI ₃	1.071	1.461	195.7
CH(OCH ₃) ₃	1.070	1.450	193.9	186 ^b	7.9

^a See ref. 4. ^b N. Muller and P. I. Rose, *J. Am. Chem. Soc.*, **84**, 3973 (1962). ^c G. S. Reddy and J. H. Goldstein, *J. Chem. Phys.*, **38**, 2736 (1963). ^d H. Spiesscke and W. G. Schneider, *ibid.*, **35**, 722 (1961). ^e See ref. 6. ^f (CH₃)₂O, 140^b; CH₃OH, 141^a; CH₃-OC₆H₅, 143^a; *p*-CH₃OC₆H₄CHO, 145^a; (CH₃O)₂CCH₂, 147^a. ^g Not available. ^h See ref. 5.

Values of Q_K for a carbon-halogen bond are estimated with bond dipole moments from Moelwyn-Hughes¹⁰ from the proportional relationship $(\mu_K R_{\text{CH}}/\mu_{\text{CH}} R_K) Q_{\text{CH}}$, where μ_K and R_K are the bond dipole moment and bond distance, respectively, of the Kth bond. These Q_K values then are used to obtain λ_K , S_K , N_K , and Z_K . While relatively small changes in Z_K are realized for the degree of bond polarization assumed here, significant effects on ${}^{(1)}J(K)$ result from this third-power correction as observed in Table I for the various halogenated methanes. For the purposes of this treatment, the ratios $\Delta_{\text{CH}_4}/\Delta_K$ and $(\alpha_K/\alpha_{\text{CH}_4})^2$ are assumed to be unity in the predicted values given in Table I.

The agreement between calculated and experimental coupling constants may be improved by the inclusion of Δ and α^2 . It is shown, however, that reasonable changes in the effective nuclear charge can account for

(8) C. A. Coulson, *Trans. Faraday Soc.*, **38**, 433 (1942).

(9) A. value of 0.33 is required to fit a C-H bond dipole moment of 0.4 D. (see ref. 8). Coulson has indicated, however, that a 0.33 value is probably too large.

(10) E. A. Moelwyn-Hughes, "Physical Chemistry," 2nd Revised Ed., Pergamon Press, New York, N. Y., 1961, p. 530.

(1) M. Karplus and D. M. Grant, *Proc. Natl. Acad. Sci. U. S.*, **45**, 1269 (1959).
(2) C. Juan and H. S. Gutowsky, *J. Chem. Phys.*, **37**, 2198 (1962).
(3) J. N. Shoolery, *ibid.*, **31**, 1427 (1959).
(4) N. Muller and D. E. Pritchard, *ibid.*, **31**, 768, 1471 (1959).
(5) N. Muller, *ibid.*, **36**, 359 (1962).
(6) E. R. Malinowski, *J. Am. Chem. Soc.*, **83**, 4479 (1961).
(7) H. S. Gutowsky and C. S. Juan, *ibid.*, **84**, 307 (1962).

the general changes observed in ${}^1J_{C_{18}-H}$ and that very large changes in the hybridization parameters are not required, as assumed earlier, to fit the experimental couplings in these near tetrahedral systems. The substituent parameters of Malinowski⁶ also may be explained better by additive incremental changes in $(Z_K)^3$ for a substituted carbon atom. Cautious application of hybridization criteria for molecules which have similar geometry is recommended until variations in the effective nuclear charge upon the radial wave function of a substituted carbon atom are better understood.

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David M. Grant, William M. Litchman
Department of Chemistry, University of Utah
Salt Lake City, Utah 84112
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A Correlation of F^{19} - F^{19} *gem* Coupling Constants with Chemical Shifts in the Nuclear Magnetic Resonance Spectra of Fluoroalkenes

Sir:

The geometrical relationship between any two fluorine atoms in a polyfluoroalkene molecule can often be determined by the magnitude of the spin-spin coupling constants obtained from the F^{19} n.m.r. spectrum. Values of J^{FF}_{trans} are distinctive, being more than 110 c.p.s.,¹ and provide a ready means for the proper assign-

Table I. Chemical Shifts^a and Fluorine-Fluorine *gem* Coupling Constants for $F_1F_2C=CX_1X_2$

	Compd.		δ_{F_1} , p.p.m.	δ_{F_2} , p.p.m.	$J^{F_1F_2}_{gem}$, c.p.s.	Ref.
	X_1	X_2				
1	F	H	101.6	129.4	87	b, c
2	F	CF=CFY ^d	107	119	82	e
3	F	Cl	105	121	78	c, f
4	F	CF ₂ Y ^e	104	112	72	e
5	F	Br	96.4	116.8	71.3	b
6	F	CF ₃	93	107	57	h
7	F	CF ₂ Cl	95	106	56	h
8	F	CF ₂ Br	95.3	105.4	55.0	i
9	F	CF ₂ I	95.0	104.1	53.4	i
10	H	CH=CF ₂	$1/2(\delta_{F_1} + \delta_{F_2}) = 87.6$		36.6	j, k
11	H	H	81.3	81.3	36.4	b, l
12	Br	H	81.9	82.8	34.5	b
13	CF ₃	Cl	78.2	78.5	16.7	m
14	F	COF	77.1	88.8	6.6	i

^a Chemical shifts are given relative to CCl₃F. ^b J. Reuben, Y. Shvo, and A. Demiel, to be published. ^c Reference 1. ^d Y = Ni(Ph₃P) π -C₆H₆. ^e D. W. McBride, E. Dudek, and F. G. A. Stone, *J. Chem. Soc.*, 1752 (1964). ^f Reference 3. ^g Y = Ni(CO) π -C₆H₆. ^h E. Pitcher and F. G. A. Stone, *Spectrochim. Acta*, **17**, 1244 (1961). ⁱ Reference 4. ^j J. L. Anderson, R. E. Putnam, and W. H. Sharkey, *J. Am. Chem. Soc.*, **83**, 382 (1961). ^k K. L. Servis and J. D. Roberts, *ibid.*, **87**, 1339 (1965). ^l G. W. Flynn and J. D. Baldeschwieler, *J. Chem. Phys.*, **38**, 226 (1963). ^m Reference 5.

ment of the correct geometrical configuration.² Both *gem* and *cis* F^{19} - F^{19} coupling constants are, however, spread over wide and overlapping ranges. In some

(1) H. M. McConnell, C. A. Reilly, and A. D. McLean, *J. Chem. Phys.*, **24**, 479 (1956).

(2) See, for example, D. Seyferth and T. Wada, *Inorg. Chem.*, **1**, 78 (1962).

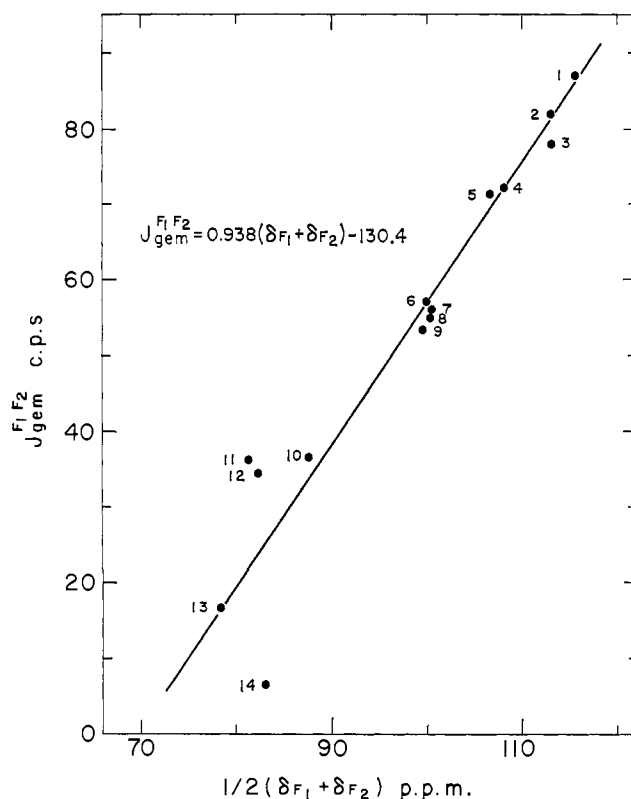


Figure 1. A plot of $J^{F_1F_2}_{gem}$ vs. the mean chemical shift of the interacting nuclei for compounds of the type $F_1F_2C=CX_1X_2$. Numbers refer to Table I.

cases, as¹ in $F_2C=CFH$, $F_2C=CFBr$, $F_2C=CFCl$, etc., J^{FF}_{gem} is greater than J^{FF}_{cis} . In other instances, as in $F_2C=CFCN$,¹ $F_2C=CFBCl_2$,³ and $F_2C=CFCOF$,⁴ the inverse relation has been found, J^{FF}_{gem} being smaller than J^{FF}_{cis} . The ambiguity thus arising is most disturbing when F^{19} - F^{19} coupling constants are used for the elucidation of molecular structure.

In Table I n.m.r. data compiled from the literature and completed with some of our measurements are presented for fluoroalkenes containing a 1,1-difluorovinyl radical.

Low values of J^{FF}_{gem} have been noted by several authors,³⁻⁵ but no satisfactory explanation has been offered. In molecules bearing a mesomerically electron-withdrawing group, bonded to 1,1-difluorovinyl, the contribution of valence-bond resonance structures, such as $F_2C^+-CF=C=N^-$, $F_2C^+-CF=B-Cl_2$, $F_2C^+-CF=CF-O^-$, have to be considered. By this mechanism electrons are removed from the terminal carbon atom, and if these carry nuclear spin information the *gem* coupling constant between the fluorine atoms bound to it will be reduced. At the same time a decreased shielding of the interacting nuclei is expected. Mesomerically electron-releasing substituents will have an opposite effect, owing to contributions of resonance forms of the type $F_2C^--CF=X^+$.

From the above considerations a direct relationship between the magnitude of the coupling constants and the chemical shifts of the geminal fluorines may be anticipated. In Figure 1 J^{FF}_{gem} is plotted vs. the mean

(3) T. D. Coyle, S. L. Stafford, and F. G. A. Stone, *Spectrochim. Acta*, **17**, 968 (1961).

(4) K. C. Ramey and W. S. Brey, Jr., *J. Chem. Phys.*, **40**, 2349 (1964).

(5) J. D. Swalen and C. A. Reilly, *ibid.*, **34**, 2122 (1961).