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¹³C-H Coupling Constants. II.* Periodic Table Variation of $J^{13}\text{C-H}$ and Carbon Hybridization Effects on Its Value

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NUMEROUS authors¹ have dealt with the factors influencing carbon-13-proton coupling constants. Many have held that variations in carbon orbital hybridization were solely responsible for variations of $J^{13}\text{C-H}$ from molecule to molecule. More recently, however, others² have pointed out that substituent effects may be explained without recourse to "s-

orbital affinity" or "p-orbital affinity" of the substituent, and the work of Moffitt³ supports this conclusion.

It seems reasonable that large differences in s character of the carbon hybrid orbital used in forming C-H bonds will cause large variations in $J^{13}\text{C-H}$, for example, in the series C₂H₆, C₂H₄, and C₂H₂.^{1a,1c,4} However, it may be quite unreasonable to state that large changes in $J^{13}\text{C-H}$ indicate large changes in s character in, for example, the series (CH₃)₄C through CH₃F.

Large variation in the size of the substituent also apparently causes variations in $J^{13}\text{C-H}$. Muller and Pritchard^{1b} attributed this to a demand for carbon p character by the substituent, due to the fact that larger substituents, with more diffuse bonding orbitals, can achieve better overlap with carbon if the carbon atom offers a hybrid with a large p character.^{1b,5}

Ranft^{1j} has given equations isolating the dependence of $J^{13}\text{C-H}$ on electronegativity, with the same coefficient for all atomic periods, but he interprets all variation in $J^{13}\text{C-H}$ as due to changes in carbon hybridization.

The data presented in Table I and Fig. 1 have been gathered from various references and from measurements made in this laboratory. The points on Fig. 1 are numbered as shown in the table.

Overlap effects causing variation in $J^{13}\text{C-H}$ via

TABLE I. Electronegativities, bond lengths, and coupling constants.

No.	Substituent	Pauling electroneg. of central atom	$J^{13}\text{C-H}$	J Ref.	$r_{\text{CX}}(\text{\AA})^*$
1	-F	4.0	149.1±0.2	a	1.38 ₈
2	-OMe	3.5	139.6±0.4	a	1.42±0.03
3	-NMe ₂	3.0	131±1	b	1.47±0.02
4	-CMe ₃	2.5	124.5±0.1	c	1.54±0.02
5	-Li	1.0	98(±1)	d	...
6	-Cl	3.0	150±1	b	1.78 ₁ ±0.005
7	-SMe	2.5	137.5±0.1	c	1.82±0.03
8	-SiMe ₃	1.8	118.2±0.1	c	1.88 ₈ ±0.02
9	-Al ₂ Me ₅	1.5	113(±1)	f	1.99, 2.00 ¹
10	-MgX	1.2	107.7(±1)	g	(2.15)
11	-Br	2.8	152±1	b	1.93 ₉
12	-SeMe	2.4	140.2±0.5	h	(1.93)
13	-GeMe ₃	1.8	124.0±0.4	e	1.98±0.03
14	-GaMe ₂	1.6	122(±1)	f	(2.02)
15	-I	2.5	151.0±0.1	c	2.13 ₉
16	-TeMe	2.1	140.5(±1)	i	(2.12)
17	-SnMe ₃	1.8	127.2±0.1	e	2.18±0.03
18	-InMe ₂	1.7	126(±1)	f	2.16±0.04
19	-PbMe ₃	1.8	134.0±0.2	e	2.29±0.05
20	-H	2.1	125±1	j	...

* Reference 1(i).

^b Reference 1(b).

^c This work.

^d T. L. Brown, R. L. Gerteis, D. A. Bafus, and J. A. Ladd, J. Am. Chem. Soc. **86**, 5125

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^k Bond-length references: *Tables of Interatomic Distances and Configuration in Molecules and Ions*, L. E. Sutton, Ed. (The Chemical Society, London, 1958). Values in parentheses estimated from covalent radii, in L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, N. Y., 1960), 3rd ed., pp. 93, 246, 382, 383.

¹ The Al-C bond length for nonbridging CH₃ groups. For bridging CH₃ groups, $r_{\text{Al-C}}=2.24$ Å.

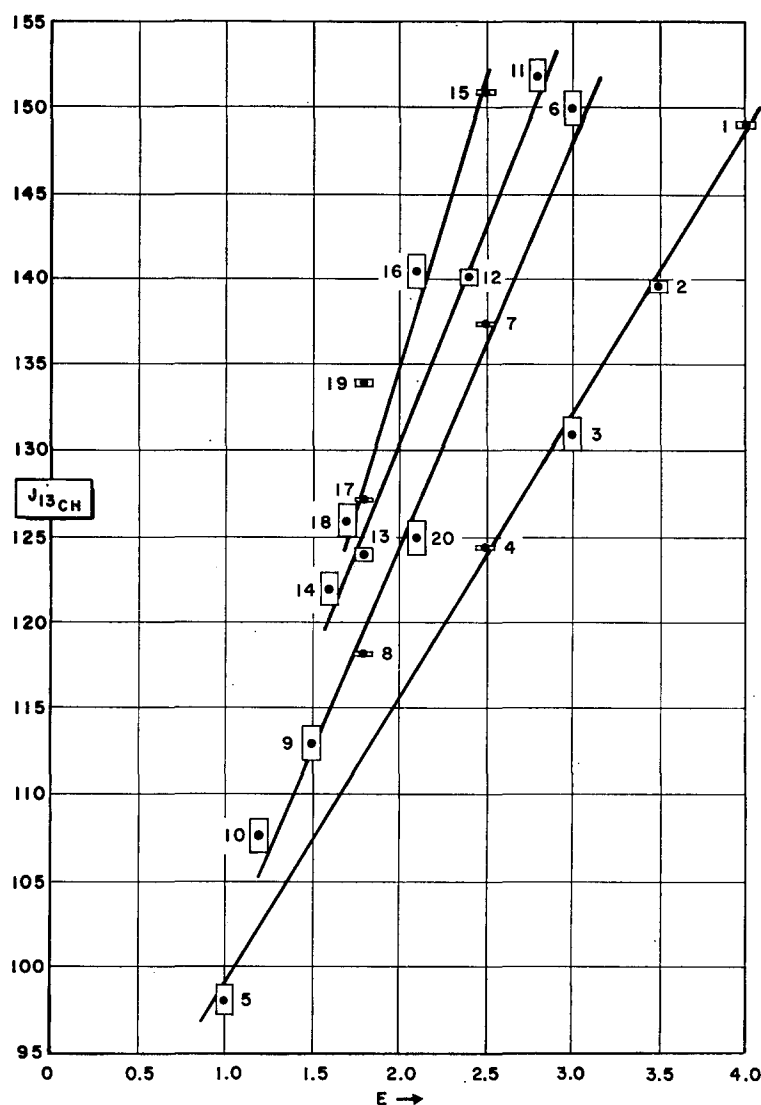


FIG. 1. J_{13C-H} in monosubstituted methanes plotted vs Pauling electronegativity, showing separate straight-line correlations for each of the atomic periods two through five. The boxes surrounding each point include the error range in both the coupling (as reported in the reference cited) and the electronegativity values, assumed accurate to ± 0.05 units. Where no error range for a coupling was reported, an assumed range of ± 1.0 cps has been employed, as indicated by parentheses about the error figure in Table I.

hybridization changes are implied in two ways in Fig. 1. First, the offset of a plot, for an atomic period of larger principal quantum number, to higher values of J_{13C-H} , parallels the increase in average carbon-to-substituent bond lengths for each period, in agreement with the overlap rationale.^{1b,5}

Secondly, the fact that the four linear plots of J_{13C-H} vs electronegativity have different slopes further supports the thesis that hybridization changes are important in determining J_{13C-H} since the relative change of C-X bond length is largest in Period 2 and least in Period 5. These relative changes in bond length, tending to cancel effects of increases in electronegativity on J_{13C-H} , give the smallest slope in the Period 2 plot, and the greatest slope for Period 5.

While convincing arguments show that factors other than carbon hybridization variations may account for all or part of the observed variations in $^{13}C-H$ coupling

constants, the evidence accumulated here suggests that one must not now omit all consideration of the importance of changes in hybridization. It is important here, however, that no assumption is made that "affinities" of a substituent for "more loosely bound" p electrons control hybridization variations. I rely on the much more reasonable postulate that the demand for maximum overlap is responsible, as reflected in the effects of bond length variation. These results, with those in Ref. 5(a) and 5(b), support the original statement of this postulate^{1b} and enhance the argument with their general coverage of substituents.

* Paper I is "Consistent Deviations from Nonadditivity of Substituent Effects on $^{13}C-H$ Coupling Constants," by A. W. Douglas, *J. Chem. Phys.* **40**, 2413 (1964).

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Signs of the Rotational Magnetic Moment and Electric Dipole Moment of CO

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THE first to use the isotopic change in molecular g factor to determine the sign of the electric dipole moment of a molecule were Rosenblum, Nethercot, and Townes (RNT).¹ The relationship used is^{1,2}

$$I'g' - Ig = -2\Delta\mu M/e, \quad (1)$$

where I' , I are the moments of inertia of the nuclei in two isotopes of the molecule; g' , g are the respective g factors for rotation about an axis perpendicular to the molecular axis and through the center of mass; Δ is the separation of the centers of mass in the two isotopes; μ is the electric dipole moment; M is the proton mass; and e is the electronic charge. The sign conventions are such that Δ is positive if the primed center of mass is to the right of the unprimed, μ positive means $-+$ left-right polarity of the dipole moment, and the nuclear component of the g factor is positive. Equation (1) is derived for a neutral, linear, closed-shell molecule ignoring vibrational and centrifugal effects.² The use of Eq. (1) is the only technique suggested so far, outside of direct computation, capable of determining the sign of the dipole moment (more precisely, the relative signs of g and μ). If sufficiently precise measurements of g are available, it is necessary to include vibrational corrections for quantitative determinations of the magnitude of the dipole moment.³

In determining the sign of μ in CO, RNT argued that the sign of g was most probably negative and, with this choice, modified the observed rotational magnetic moments to eliminate contributions arising from the dipole moment according to Eq. (1). They showed that assuming a C^-O^+ polarity for μ gave a modified rotational magnetic moments which were a monotonic function of the rotational frequency (whereas this is not the case with a C^+O^- polarity) and interpreted this as a determination of a C^-O^+ polarity. Combined with an independent determination of the

magnitude of μ , the experimental value is 0.112 ± 0.005 D, C^-O^+ .⁴

Recent molecular orbital calculations,⁵⁻⁷ converging on the Hartree-Fock wavefunction for CO, show that for this type of wavefunction the computed dipole moment at the experimental equilibrium separation of 1.128 Å is 0.26 ± 0.02 D, C^+O^- .⁷ At the computed equilibrium separation this is probably decreased in magnitude by 0.12 D, still preserving the C^+O^- polarity.⁸ In view of the closer agreement between other similar calculations and experiment, particularly for HF⁹ and LiF,¹⁰ Nesbet⁵ undertook a critical review of RNT's determination of the sign of μ . (In both of these molecules the difference between Hartree-Fock dipole moment and the observed one is less than 0.1 D.) His review focused on the magnitude of corrections to the rotational constant B_e of the molecule, as follows. In computing isotopic mass ratios it is necessary to obtain the rotational constant corresponding to an idealized molecule consisting of nuclei with the same separations but surrounded by spherical shells of electrons.¹ To do this, two corrections to the observed B_e are made. The first is due to the actual moment of inertia of the electrons and is obtained from the observed g factor. The second contains the wobble-stretching term as its most important component, and is estimated empirically by selecting a value which gives precise agreement with one independently obtained isotopic mass ratio. In the RNT analysis which uses negative g factors, the wobble-stretching correction is of the same sign and an order of magnitude smaller than the correction due to the electronic moment of inertia. Nesbet pointed out that the RNT results for isotopic mass ratios would still be in excellent agreement with independent observations of these ratios using a positive g factor, if the wobble-stretch correction was an order of magnitude larger.

Our contribution to the subject is to confirm the negative sign on the g factor for CO, thereby confirming the C^-O^+ polarity of the dipole moment, and also that the wobble-stretching correction is an order of magnitude smaller than that due to the electronic moment of inertia. This is done by utilizing the relationship¹¹

$$\xi = (-e^2/6mc^2)[\langle r^2 \rangle + (Ig/M) - (\sum_k Z_k d_k^2/e)], \quad (2)$$

between the diamagnetic susceptibility ξ and the g factor in a linear closed-shell molecule. In Eq. (2), $\langle r^2 \rangle$ is the expectation value of r^2 measured from the center of mass, summed over the electrons; I the nuclear moment of inertia about the center of mass; Z_k are the nuclear charges; d_k the distance of nucleus k from the center of mass; and \sum_k is over the nuclei. e , m , c , and M are, respectively, the electron charge, electron mass, velocity of light, and proton mass. Using a computed value of 39.8468 a.u.⁸ for $\langle r^2 \rangle$ and deter-