

# Proton-<sup>13</sup>C Spin-Spin Coupling. VI. Factors Affecting $J_{13\text{CCH}}$ . The $(\text{CH}_3)_3\text{C}^{13}\text{C}$ System

Gerasimos J. Karabatsos<sup>1</sup> and Chester E. Orzech, Jr.<sup>2</sup>

Contribution from the Kedzie Chemical Laboratory, Michigan State University, East Lansing, Michigan. Received July 27, 1964

Proton-<sup>13</sup>C coupling constants through three bonds,  $J_{13\text{CCH}}$ , were determined for 42 compounds of the general structure  $(\text{CH}_3)_3\text{C}^{13}\text{C}$ . The couplings ranged from 3.59 to 5.99 c.p.s. for  $sp^3$ -hybridized <sup>13</sup>C, and from 3.72 to 6.43 c.p.s. for  $sp^2$ -hybridized <sup>13</sup>C. A value of 5.38 c.p.s. was obtained for trimethylacetone (sp-hybridized <sup>13</sup>C). Strong nonbonded repulsions among the groups attached to the <sup>13</sup>C led to low couplings; halogen substituents on the <sup>13</sup>C led to high couplings. The data are interpreted in terms of substituent electronegativity (increase in the electronegativity of the substituent on the <sup>13</sup>C increases  $J_{13\text{CCH}}$ ) and in terms of angle and bond deformations. The possibility that conformational differences between the various compounds might be responsible for the variations in  $J_{13\text{CCH}}$  was examined and rejected.

Several investigations have been directed toward elucidation of the factors affecting proton-<sup>13</sup>C coupling. The short-range coupling,  $J_{13\text{CH}}$ , has been studied extensively.<sup>3</sup> The general linearity between  $J_{13\text{CH}}$  and fractional s-character of the <sup>13</sup>C hybrid atomic orbital has led to the conclusion that the Fermi contact term is essentially the sole contributor to the coupling, as suggested from valence bond theory.<sup>4</sup> Additivity relations of substituent effects on  $J_{13\text{CH}}$  in substituted methanes<sup>3f</sup> and formyl compounds<sup>3g</sup> have been discovered. For the former compounds this additivity has been derived and interpreted from valence bond theory,<sup>3h</sup> with eq. 1 expressing the relation between

$$J_{13\text{CH}} = 500\alpha_{\text{H}}^2 \text{ c.p.s.} \quad (1)$$

$J_{13\text{CH}}$  and fractional s-character ( $\alpha_{\text{H}}^2$ ) of the carbon hybrid orbital used in the <sup>13</sup>C-H bond. Deviations from the additivity relations have been observed<sup>3e,k,l</sup> and empirical corrections have been suggested.<sup>3i</sup> Recently, the validity of s-characters calculated from experimental  $J_{13\text{CH}}$  has been questioned.<sup>5</sup> The finding<sup>6</sup>

(1) Fellow of the Alfred P. Sloan Foundation.

(2) National Science Foundation Predoctoral Cooperative Fellow, 1962-1964.

(3) (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); (i) H. Dreesskamp and E. Sackmann, *Z. Physik. Chem. (Frankfurt)*, **27**, 136 (1961); **34**, 273 (1962); (j) J. Ranft, *Ann. Physik*, **9**, 124 (1962); **10**, 399 (1963); (k) S. G. Frankiss, *J. Phys. Chem.*, **67**, 752 (1963); (l) A. W. Douglas, *J. Chem. Phys.*, **40**, 2413 (1964); (m) C. S. Foote, *Tetrahedron Letters*, **9**, 579 (1963); (n) K. Mislow, *ibid.*, **22**, 1415 (1964); (o) G. P. van der Kelen and Z. Eeckhut, *J. Mol. Spectry.*, **10**, 141 (1963).

(4) M. Karplus and D. Grant, *Proc. Natl. Acad. Sci. U. S.*, **45**, 1269 (1959).

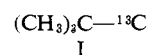
(5) G. J. Karabatsos and C. E. Orzech, Jr., *J. Am. Chem. Soc.*, **86**, 3574 (1964).

(6) G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre, and I. J. Bastien, *ibid.*, **86**, 1360 (1964).

that for the isopropyl cation,  $(\text{CH}_3)_2^{13}\text{CH}^+$ ,  $J_{13\text{CH}}$  is 382 c.p.s.—which would imply more than 0.75 s-character for the carbon atomic orbital used in the <sup>13</sup>C-H bond—casts further doubt on such s-characters.

Long-range proton-<sup>13</sup>C coupling has enjoyed less attention than  $J_{13\text{CH}}$ . From an approximate treatment of  $J_{13\text{CCH}}$ , and the linearity between  $J_{13\text{CCH}}$  and fractional s-character of the <sup>13</sup>C hybrid atomic orbital, it was concluded<sup>7</sup> that contact interaction dominates this coupling when  $\angle^{13}\text{CCH}$  is tetrahedral. The same conclusion was reached in more recent publications.<sup>3j,8</sup> No simple correlation was found between the three-bond coupling,  $J_{13\text{CCH}}$ , and the s-character of the <sup>13</sup>C atomic orbital.<sup>9</sup>

Elucidation of the factors affecting long-range proton-<sup>13</sup>C coupling has been hampered by lack of sufficient and pertinent data. We have undertaken, therefore, a general study of long-range coupling in order to assess the relative importance of the various factors. In this paper we shall discuss  $J_{13\text{CCH}}$  calculated from compounds of structure I. The choice of such compounds was dictated by convenience and by the simplicity inherent in first-order spectra.



## Results

Table I summarizes pertinent coupling constants that were obtained with an A-60 spectrometer at about 36°. The values for the long-range constants, determined at sweep widths of 50 c.p.s., are averages of at least three measurements with precision of  $\pm 0.03$  c.p.s. They were checked against the coupling of acetaldehyde,  $J_{\text{HH}} = 2.85$  c.p.s., and should be accurate to  $\pm 0.05$  c.p.s. Short-range constants, determined at sweep widths of 250 c.p.s., are also averages of at least three determinations with precision of  $\pm 0.2$  c.p.s. They should be accurate to  $\pm 0.5$  c.p.s.

All spectra had simple, first-order appearance. Neopentyl sulfite and chlorosulfite, as a consequence of nonplanar sulfur, showed nonequivalent methylene protons.<sup>10</sup>

## Discussion

The extensive variation of  $J_{13\text{CCH}}$  (from 3.59 to 5.99 c.p.s. when the <sup>13</sup>C is  $sp^3$  hybridized, 3.72 to 6.43 c.p.s. when  $sp^2$  hybridized, and the value of 5.38 c.p.s. when  $sp$  hybridized) clearly indicates that in addition to the

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

(8) G. W. Smith, *J. Chem. Phys.*, **39**, 2031 (1963); **40**, 2037 (1964).

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

(10) For magnetically nonequivalent methylene protons of sulfites see: H. Finegold, *Proc. Chem. Soc.*, 283 (1960); F. Kaplan and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 4666 (1961); J. G. Pritchard and P. C. Lauterbur, *ibid.*, **83**, 2105 (1961).

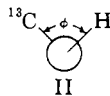
Table I. Proton-<sup>13</sup>C Couplings Calculated from (CH<sub>3</sub>)<sub>3</sub>C<sup>13</sup>C Compounds<sup>a</sup>

Compd. <sup>b</sup>	$J_{^{13}\text{CCH}}$ (c.p.s.)	$J_{^{13}\text{CH}}$ (c.p.s.)
1. R <sup>13</sup> CH <sub>3</sub>	4.65	123.3
2. R <sup>13</sup> CH <sub>2</sub> CD <sub>2</sub> OH	4.13	124.0
3. R <sup>13</sup> CH <sub>2</sub> CD <sub>2</sub> OAc	4.21	127.2
4. R <sup>13</sup> CH <sub>2</sub> CD <sub>2</sub> Br	4.36	131.0
5. R <sup>13</sup> CH <sub>2</sub> CO <sub>2</sub> H	4.44	126.4
6. R <sup>13</sup> CH <sub>2</sub> OH	4.48 <sup>a,c,d</sup>	139.9
7. R <sup>13</sup> CH <sub>2</sub> OAc	4.83	146.1
8. R <sup>13</sup> CH <sub>2</sub> OCOC <sub>6</sub> H <sub>4</sub> OCH <sub>2</sub> - <i>p</i>	4.74	145.7
9. R <sup>13</sup> CH <sub>2</sub> OCOC <sub>6</sub> H <sub>5</sub>	4.81	146.1
10. R <sup>13</sup> CH <sub>2</sub> OCOC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> - <i>p</i>	4.91	146.8
11. R <sup>13</sup> CH <sub>2</sub> OTs	5.17	147.9
12. (R <sup>13</sup> CH <sub>2</sub> O) <sub>2</sub> SO	5.16	146.3
13. R <sup>13</sup> CH <sub>2</sub> OSOCI	5.42	150.0
14. R <sup>13</sup> CH <sub>2</sub> OSi(CH <sub>3</sub> ) <sub>2</sub>	4.79	139.3
15. R <sup>13</sup> CH <sub>2</sub> N <sup>+</sup> H <sub>3</sub> ClO <sub>4</sub> <sup>-</sup>	5.01 <sup>e</sup>	143.0
16. R <sup>13</sup> CH <sub>2</sub> Cl	5.63	147.9
17. R <sup>13</sup> CH <sub>2</sub> Br	5.84	149.1
18. R <sup>13</sup> CH <sub>2</sub> I	5.99	148.0
19. R <sub>2</sub> <sup>13</sup> CHOH	3.80	136.8
20. R <sub>2</sub> <sup>13</sup> CHOAc	3.99	147.5
21. R <sup>13</sup> C(CH <sub>3</sub> ) <sub>2</sub> OH	3.59	
22. R <sub>2</sub> <sup>13</sup> COH	3.80	
23. R <sub>2</sub> <sup>13</sup> COAc	3.96	
24. R <sup>13</sup> CH=CD <sub>2</sub>	4.23	
25. R <sup>13</sup> C(CH <sub>3</sub> )=CH <sub>2</sub>	4.00	
26. R <sup>13</sup> CHO	4.60	171.7
27. R <sup>13</sup> COCH <sub>3</sub>	4.20	
28. R <sub>2</sub> <sup>13</sup> CO	3.72	
29. R <sup>13</sup> CO <sub>2</sub> H	4.38	
30. R <sup>13</sup> CO <sub>2</sub> <sup>-</sup> K <sup>+</sup>	4.36 <sup>e</sup>	
31. R <sup>13</sup> CO <sub>2</sub> CH <sub>3</sub>	4.11	
32. R <sup>13</sup> CO <sub>2</sub> CH <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub>	4.10	
33. R <sup>13</sup> CO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> OCH <sub>2</sub> - <i>p</i>	4.58	
34. R <sup>13</sup> CO <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	4.60	
35. R <sup>13</sup> CO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> - <i>p</i>	4.76	
36. R <sup>13</sup> CONH <sub>2</sub>	4.07	
37. R <sup>13</sup> CONHC <sub>6</sub> H <sub>5</sub>	4.38	
38. R <sup>13</sup> COCl	5.99	
39. R <sup>13</sup> COB	6.43	
40. R <sup>13</sup> CH=NNHC <sub>6</sub> H <sub>5</sub> (NO <sub>2</sub> ) <sub>2</sub>	4.40	166.2
41. R <sup>13</sup> C(CH <sub>3</sub> )=NNHC <sub>6</sub> H <sub>5</sub> (NO <sub>2</sub> ) <sub>2</sub>	3.91	
42. R <sup>13</sup> CN	5.38	

<sup>a</sup> Unless otherwise noted, spectra were taken in carbon tetrachloride solutions. <sup>b</sup> R stands for (CH<sub>3</sub>)<sub>3</sub>C. <sup>c</sup> Benzene solution. <sup>d</sup> Dimethyl sulfoxide solution. <sup>e</sup> Deuterium oxide solution.

s-character of the <sup>13</sup>C hybrid atomic orbital, other factors must significantly affect this coupling. We shall discuss some of these factors in detail.

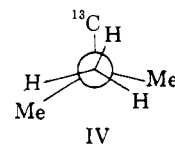
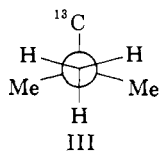
**Dihedral Angle Effect.** Although the dependence of  $J_{^{13}\text{CCH}}$  on  $\phi$  (II) has yet to be experimentally demonstrated, it is reasonable to assume that the relation



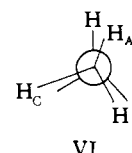
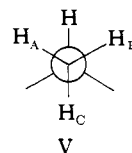
between  $J_{\text{HCCH}}$  and  $\phi$ <sup>11</sup> qualitatively applies to  $J_{^{13}\text{CCH}}$  and  $\phi$ . Any variation in the present data, however, as a result of such dependence can be readily discounted. Firstly, it is highly improbable that any of the compounds examined exists in conformations other than III. Secondly, even if extreme conformational differences (ranging from III to IV) existed between the various compounds, the experimentally determined constants should be independent of conformation.

(11) M. Karplus, *J. Am. Chem. Soc.*, **85**, 2870 (1963), and previous references by the same author.

Consider  $J_{\text{HCCH}}$  of a CH<sub>3</sub>CH group as the conforma-



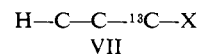
tion varies from V (staggered) to VI (eclipsed). Using



eq. 2<sup>11</sup> one finds that the average coupling,  $J_{\text{HH}}$  (av.) = ( $J_{\text{HH}_A} + J_{\text{HH}_B} + J_{\text{HH}_C}$ )/3, is independent of conformation.

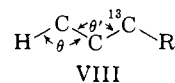
$$J_{\text{HH}'} = A + B \cos \phi + C \cos 2\phi \quad (2)$$

**Substituent Electronegativity Effect.** When the substituent is bonded to the <sup>13</sup>C, the effect of its electronegativity on  $J_{^{13}\text{CCH}}$  can be readily predicted, e.g., increase in the electronegativity of X (VII) should in-



crease  $J_{^{13}\text{CCH}}$  by virtue of increasing the s-character<sup>12</sup> of the <sup>13</sup>C atomic orbital used in the <sup>13</sup>C-C bond. The values obtained from the *para*-substituted neopentyl benzoates (entries 8, 9, and 10 in Table I) and phenyl pivalates (entries 33, 34, and 35), where the effects of factors other than electronegativity are kept constant, bear out this prediction. The contribution of electronegativity, however, can be readily masked by the effects of other factors.

**Angle  $\theta$  and  $\theta'$  Effect.** Vicinal proton-proton couplings,  $J_{\text{HCC'H}}$ , decrease with increase in angles  $\theta$  and  $\theta'$  [ $\theta = \angle \text{HCC}'$ ,  $\theta' = \angle \text{HC}'\text{C}$ ].<sup>11,13</sup> It is reasonable to assume, therefore, that  $J_{^{13}\text{CCH}}$  might be affected similarly by changes in  $\theta$  and  $\theta'$  [ $\theta = \angle \text{HCC}$ ,  $\theta' = \angle ^{13}\text{CCC}$ ]. Although  $\theta$  and  $\theta'$  are not known for the compounds studied, reasonable guesses can be made as to what structural features might increase these angles. The most plausible feature is increase in the size of groups attached to the <sup>13</sup>C, e.g., as R increases in size (VIII),  $\theta$  and  $\theta'$  should increase on account of nonbonded repulsions. On this assumption

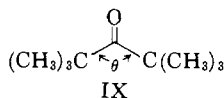


several trends and apparent inconsistencies in the data can be qualitatively accounted for. For example, compare the rather large coupling of neopentane (small repulsions) with the relatively small couplings of all other compounds (large repulsions). Specifically, compare entries (Table I) 1, 19, 21, and 22; 24 and 25; 26,

(12) H. A. Bent, *Chem. Rev.*, **61**, 275 (1961).

(13) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 195; H. S. Gutowsky and A. L. Porte, *J. Chem. Phys.*, **35**, 839 (1961); R. J. Abraham and H. J. Bernstein, *Can. J. Chem.*, **39**, 905 (1961); J. D. Graham and M. T. Rogers, *J. Am. Chem. Soc.*, **84**, 2249 (1962); O. L. Chapman, *ibid.*, **85**, 2014 (1962); G. V. Smith and H. Kriloff, *ibid.*, **85**, 2016 (1963); P. Laszlo and P. von R. Schleyer, *ibid.*, **85**, 2018 (1963).

27, and 28; and 40 and 41. From the low carbonyl stretching frequency of di-*t*-butyl ketone it was suggested<sup>14</sup> that  $\theta$  (IX) should be 130–137°. Such an angle requires an s-character of 0.39–0.42 for the <sup>13</sup>C



atomic orbital used in the <sup>13</sup>C–C bond. Assuming the <sup>13</sup>C atomic orbital of neopentane to have 0.25 s-character, and using contact interaction, a coupling constant of 7.3–7.8 c.p.s. is calculated for di-*t*-butyl ketone. The experimental value is only 3.72 c.p.s. It would seem, therefore, that  $J_{^{13}\text{C}\text{C}\text{H}}$  is extremely sensitive to  $\theta$  and  $\theta'$ .

**Bent Bonds.** Theoretical and experimental investigations have recently emphasized that the maximum electron density of a  $\sigma$ -bond may not lie along the internuclear straight line.<sup>15</sup> Although the effect of bond bending on spin–spin coupling has not been evaluated, it is reasonable to expect that it would decrease contact contribution. With respect to the present data bond bending would introduce the same effects as increases in angles  $\theta$  and  $\theta'$ .

As pointed out it is generally accepted that contact interaction dominates proton–<sup>13</sup>C coupling. Electron-orbital and spin-dipole contributions have been discarded in view of their significance only when the interacting nuclei possess angular dependent atomic orbitals (p, d, and f). Theoretical calculations<sup>16</sup> have predicted significant contributions to  $J_{\text{HF}}$  and  $J_{\text{FF}}$  via electron orbital motion. Recently some fluorine–fluorine<sup>17</sup> and proton–fluorine<sup>18</sup> couplings have been rationalized in terms of possible contributions through space.

(14) J. O. Halford, *J. Chem. Phys.*, **24**, 830 (1956).

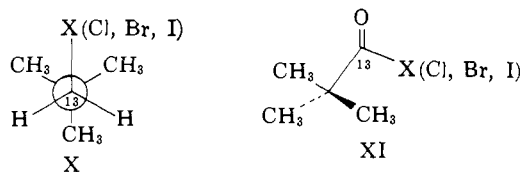
(15) D. Peters, *J. Chem. Soc.*, 2003 (1963); A. Veillard and G. Del Re, *Theoret. Chim. Acta*, **2**, 55 (1964); U. Blukis, P. H. Kasai, and R. J. Myers, *J. Chem. Phys.*, **38**, 2753 (1963); L. S. Bartell, B. L. Carroll, and J. P. Guillory, *Tetrahedron Letters*, **13**, 705 (1964); for further references see the recent review by W. H. Flygare, *Science*, **140**, 1179 (1963).

(16) J. A. Pople, *Mol. Phys.*, **1**, 216 (1958).

(17) S. Ng and C. H. Sederholm, *J. Chem. Phys.*, **40**, 2090 (1964).

(18) M. Takahashi, D. R. Davis, and J. D. Roberts, *J. Am. Chem. Soc.*, **84**, 2935 (1962); A. H. Lewin, *ibid.*, **86**, 2303 (1964).

The unusually high values for compounds having a halogen attached to the <sup>13</sup>C and the increase of these values in the order chloro < bromo < iodo, whereas from halogen electronegativities the reverse order is expected, suggest that a positive contribution to these couplings may arise from interactions (through space) between the proton magnetic moment and currents induced on the halogen atom by the <sup>13</sup>C nucleus. The close proximity between halogen and methyl protons (X and XI) might facilitate such interactions. The



validity of this suggestion, however, requires further experimental scrutiny, especially in view of theoretical predictions<sup>16</sup> that “coupling via currents induced on a third atom will always be negligible.”

**Comparison of  $J_{^{13}\text{C}\text{C}\text{H}}$  with  $J_{^{13}\text{C}\text{H}}$ .** In light of what has been discussed it is reasonable to expect that changes on the <sup>13</sup>C will affect  $J_{^{13}\text{C}\text{C}\text{H}}$  and  $J_{^{13}\text{C}\text{H}}$  differently. Notice that for *para*-substituted neopentyl benzoates (where contributions of factors other than electronegativity are kept constant)  $J_{^{13}\text{C}\text{C}\text{H}}$  and  $J_{^{13}\text{C}\text{H}}$  vary linearly with each other.

## Experimental

**Synthesis of Labeled Compounds.** All <sup>13</sup>C-labeled compounds were prepared by conventional synthetic techniques. Trimethylacetic-1-<sup>13</sup>C acid and di-*t*-butyl ketone carbonyl-<sup>13</sup>C, prepared from the carbonation of *t*-butyl lithium with carbon dioxide-<sup>13</sup>C at –50°, served as starting materials for all other compounds.

All *n.m.r.* spectra were determined at 60 Mc. on a Model A-60 spectrometer (Varian Associates, Palo Alto, Calif.), at a temperature of about 36°. Undegassed solutions were used.

**Acknowledgment.** We thank the United States Atomic Energy Commission for financial support, Grant COO-1189-16.