FEB 15 1965

SEP 16 1965

Scheduled for February 1965, JACS.

000-1189-16

12774

[Contribution from the Kedzie Chemical Laboratory, Michigan State University,
East Lansing, Michigan]

MASTER COPY

VI.
PROTON-¹³C SPIN-SPIN COUPLING. ~~VII~~ FACTORS AFFECTING

$J_{13}^{13}\text{CCCH}$; THE $(\text{CH}_3)_3\text{C}^{13}\text{C}$ SYSTEM.

by

RELEASED FOR ANNOUNCEMENT

IN NUCLEAR SCIENCE ABSTRACTS

Gerasimos J. Karabatsos¹ and Chester E. Orzech, Jr.²

-
- (1) Fellow of the Alfred P. Sloan Foundation
(2) National Science Foundation Predoctoral Cooperative Fellow, 1962-64.
-

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:
A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.
As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

This paper was submitted for publication in the open literature at least 6 months prior to the issuance date of this Microcard. Since the U.S.A.E.C. has no evidence that it has been published, the paper is being distributed in Microcard form as a preprint.

FEB 16 1965

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Proton- ^{13}C coupling constants through three bonds, J_{13}^{CCCH} , were determined for forty-two compounds of the general structure $(\text{CH}_3)_3\text{C}-^{13}\text{C}$. The couplings ranged from 3.59-5.99 c.p.s. for sp^3 hybridized ^{13}C , and from 3.72-6.43 c.p.s. for sp^2 hybridized ^{13}C . A value of 5.38 c.p.s. was obtained for trimethylacetonitrile (sp hybridized ^{13}C). Strong nonbonded repulsions among the groups attached to the ^{13}C led to low couplings; halogen substituents on the ^{13}C led to high couplings.

The data are interpreted in terms of substituent electronegativity -- increase in the electronegativity of the substituent on the ^{13}C increases J_{13}^{CCCH} ; in terms of angle and bond deformations; and in terms of positive contributions from electron-orbital and spin-dipole interactions.

The possibility that conformational differences between the various compounds might be responsible for the variations in J_{13}^{CCCH} was examined and rejected.

Several investigations have been directed towards elucidation of the factors affecting proton- ^{13}C coupling. The short range coupling, $J_{^{13}\text{CH}}$, has been studied extensively³. The general linearity between $J_{^{13}\text{CH}}$ and ^{13}CH

-
- (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. Dreeskamp and E. Sackmann, Z. Physik. Chem., 27, 136 (1961); ibid., 34, 273 (1962); (j) J. Ranft, Ann. Physik., 9, 124 (1962); ibid., 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. Eeckhaut, J. Mol. Spec., 10, 141 (1963).
-

fractional s character of the ^{13}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 theory⁴. Additivity relations of

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

substituent effects on $J_{^{13}\text{CH}}$ in substituted methanes^{3f} and formyl compounds^{3g} have been discovered. For the former compounds this additivity has been

derived and interpreted from valence bond theory^{3h}, with equation (1) express-

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

ing the relation between $J_{13_{CH}}$ and fractional s character (α_H^2) of the carbon hybrid orbital used in $^{13}C-H$. Deviations from the additivity relations have been observed^{3e,k,l} and empirical corrections have been suggested^{3l}. Recently, the validity of s characters calculated from experimental $J_{13_{CH}}$ has been questioned⁵. The finding⁶ that for the isopropyl cation,

(5) G. J. Karabatsos and C. E. Orzech, Jr., J. Am. Chem. Soc., 86, 0000, 0000 (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).

$(CH_3)_2^{13}CH^+$, $J_{13_{CH}}$ is 382 c.p.s. -- which would imply more than 0.75 s character for the carbon atomic orbital used in the $^{13}C-H$ -- casts further doubt on such s characters.

Long range proton- ^{13}C coupling has enjoyed less attention than $J_{13_{CH}}$. From an approximate treatment of $J_{13_{CCH}}$, and the linearity between $J_{13_{CCH}}$ and fractional s character of the ^{13}C hybrid atomic orbital, it was concluded⁷

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

that contact interaction dominates this coupling when $\angle^{13}CCH$ is tetrahedral. The same conclusion was reached in more recent publications^{3j,8}. No simple

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

correlation was found between the three bond coupling, $J_{13}^{9\text{CCCH}}$, and the s character of the ^{13}C atomic orbital.

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

Elucidation of the factors affecting long range proton- ^{13}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 $J_{13}^{9\text{CCCH}}$ calculated from compounds of structure I. The choice of such compounds was dictated by convenience and by the simplicity inherent in first order spectra.

I

Results

Table I summarizes pertinent coupling constants that were obtained with an A-60 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 ± 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 ± 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 ± 0.2 c.p.s. They should be accurate to ± 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 protons¹⁰.

(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).

Discussion

The extensive variation of $J_{^{13}\text{CCHH}}$ -- from 3.59-5.99 c.p.s. when the ^{13}C is sp^3 hybridized; 3.72-6.43 c.p.s. when sp^2 hybridized; and the 5.38 c.p.s. value when sp hybridized -- clearly indicates that in addition to the s character of the ^{13}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 $J_{^{13}\text{CCHH}}$ on $\phi(\text{II})$ has yet to be experimentally demonstrated, it is reasonable to assume that the

relation between J_{HCCH} and ϕ^{11} qualitatively applies to $J_{^{13}\text{CCHH}}$ and ϕ .

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

Table I

Proton- ^{13}C Couplings Calculated from $(\text{CH}_3)_3\text{C}-^{13}\text{C}$ Compounds^a.

Compound	$J_{^{13}\text{CCH}}$ (c.p.s.)	$J_{^{13}\text{CH}}$ (c.p.s.)
1. $\text{R}-^{13}\text{CH}_3$	4.65	123.3
2. $\text{R}-^{13}\text{CH}_2\text{CD}_2\text{OH}$	4.13	124.0
3. $\text{R}-^{13}\text{CH}_2\text{CD}_2\text{OAc}$	4.21	127.2
4. $\text{R}-^{13}\text{CH}_2\text{CD}_2\text{Br}$	4.36	131.0
5. $\text{R}-^{13}\text{CH}_2\text{CO}_2\text{H}$	4.44	126.4
6. $\text{R}-^{13}\text{CH}_2\text{OH}$	4.48 ^{a,c,d}	139.9
7. $\text{R}-^{13}\text{CH}_2\text{OAc}$	4.83	146.1
8. $\text{R}-^{13}\text{CH}_2\text{OCOC}_6\text{H}_4\text{OCH}_3(\text{P/})$	4.74	145.7
9. $\text{R}-^{13}\text{CH}_2\text{OCOC}_6\text{H}_5$	4.81	146.1
10. $\text{R}-^{13}\text{CH}_2\text{OCOC}_6\text{H}_4\text{NO}_2(\text{P/})$	4.91	146.8
11. $\text{R}-^{13}\text{CH}_2\text{OTs}$	5.17	147.9
12. $(\text{R}-^{13}\text{CH}_2\text{O})_2\text{SO}$	5.16	146.3
13. $\text{Ro}-^{13}\text{CH}_2\text{OSOCl}$	5.42	150.0
14. $\text{R}-^{13}\text{CH}_2\text{OSi}(\text{CH}_3)_3$	4.79	139.3
15. $\text{R}-^{13}\text{CH}_2\text{N}^+\text{H}_3\text{ClO}_4^-$	5.01 ^e	143.0
16. $\text{R}-^{13}\text{CH}_2\text{Cl}$	5.63	147.9
17. $\text{R}-^{13}\text{CH}_2\text{Br}$	5.84	149.1
18. $\text{R}-^{13}\text{CH}_2\text{I}$	5.99	148.0
19. $\text{R}_2-^{13}\text{CHOH}$	3.80	136.8
20. $\text{R}_2-^{13}\text{CHOAc}$	3.99	147.5
21. $\text{R}-^{13}\text{C}(\text{CH}_3)_2\text{OH}$	3.59	
22. $\text{R}_3-^{13}\text{COH}$	3.80	
23. $\text{R}_3-^{13}\text{COAc}$	3.96	

Table I (Cont.)

Compound	J _{13CCCH} (c.p.s.)	J _{13CH} (C.P.S.)
24. R- ¹³ CH=CD ₂	4.23	
25. R- ¹³ C(CH ₃)=CH ₂	4.00	
26. R- ¹³ CHO	4.60	
27. R- ¹³ COCH ₃	4.20	171.7
28. R ₂ - ¹³ CO	3.72	
29. R- ¹³ CO ₂ H	4.38	
30. R- ¹³ CO ₂ K ⁺	4.36 ^e	
31. R- ¹³ CO ₂ CH ₃	4.11	
32. R- ¹³ CO ₂ CH ₂ C(CH ₃) ₃	4.10	
33. R- ¹³ CO ₂ C ₆ H ₄ OCH ₃ (P/)	4.58	
34. R- ¹³ CO ₂ C ₆ H ₅	4.60	
35. R- ¹³ CO ₂ C ₆ H ₄ NO ₂ (P/)	4.76	
36. R- ¹³ CONH ₂	4.07	
37. R- ¹³ CONHC ₆ H ₅	4.38	
38. R- ¹³ COCl	5.99	
39. R- ¹³ COBr	6.43	
40. R- ¹³ CH=NNHC ₆ H ₃ (NO ₂) ₂	4.40	166.2
41. R- ¹³ C(CH ₃)=NNHC ₆ H ₃ (NO ₂) ₂	3.91	
42. R- ¹³ CN	5.38	

^a Unless otherwise noted, spectra were taken in carbon tetrachloride solutions. ^b R stands for (CH₃)₃C. ^c Benzene solution. ^d Dimethyl sulfoxide solution. ^e Deuterium oxide solution.

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

III

IV

between the various compounds, the experimentally determined constants should be independent of conformation. Consider J_{HCCH} of a CH_3CH group as the conformation varies from V (staggered) to VI (eclipsed). Using

V

VI

equation (2)¹¹ one finds that the average coupling,

$$J_{\text{HH}} (\text{av.}) = (J_{\text{HH}_A} + J_{\text{HH}_B} + J_{\text{HH}_C})/3, \text{ is independent of conformation.}$$

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

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

VII

J_{13}^{CCCH} by virtue of increasing the s character¹² of the ^{13}C atomic orbital

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

used in the $^{13}C-C$ 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. As brought out in Figs. 1 and 2, however, the contribution of electronegativity can be readily masked by the effects of other factors.

Angle θ and θ' Effect. Vicinal proton-proton couplings, $J_{HCC'H}$, decrease with increase in angles θ and θ' [$\theta = \angle HCC'$, $\theta' = \angle HC'C$]^{11,13}. It is

(13) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance", McGraw-Hill Book Co., 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).

reasonable to assume, therefore, that J_{13}^{CCCH} might be affected similarly by changes in θ and θ' [$\theta = \angle HCC$, $\theta' = \angle C^{13}CCC$]. Although θ and θ' 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 ^{13}C ; e.g. as R increases

in size (VIII), θ and θ' should increase on account of nonbonded repulsions.

VIII

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, 27 and 28; 40 and 41. From the low carbonyl stretching frequency of di-t-butyl ketone it was suggested¹⁴ that θ (IX) should be 130-137°. Such an angle requires an s character of

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

IX

0.39-0.42 for the ^{13}C atomic orbital used in the $^{13}\text{C}-\text{C}$ bond. Assuming the ^{13}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, wherefore, that $J_{^{13}\text{C}-\text{C}}$ is extremely sensitive to θ and θ' .

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 line¹⁵. It was suggested⁵ that many apparent

-
- (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).

discrepancies in experimentally determined coupling constants may arise from such bond bending. 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 θ and θ' .

Electron-Orbital and Spin-Dipole Effect. As pointed out it is generally accepted that contact interaction dominates proton-¹³C 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, f). Theoretical calculations¹⁶ have predicted significant

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

contributions to J_{HF} and J_{FF} via electron orbital motion. Recently some fluorine-fluorine¹⁷ and proton-fluorine¹⁸ couplings have been interpreted

-
- (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).

in terms of possible contributions through space.

In an earlier communication we suggested⁵ that some proton- ^{13}C couplings could be adequately interpreted in terms of electron-orbital and/or spin-dipole contributions. Regarding the present data the pertinent observations are: unusually high values for compounds having a halogen attached to the ^{13}C ; increase of these values in the order chloro<bromo<i>iodo, whereas from halogen electronegativities the reverse order is expected. We find it difficult to rationalize these values in terms of any factor already discussed. We propose, therefore, 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 ^{13}C nucleus. The close proximity between halogen and methyl protons (X, XI) would facilitate such interactions.

The validity of this suggestion, however, requires further experimental scrutiny, in view of theoretical predictions¹⁶ that "coupling via currents induced on a third atom will always be negligible".

Comparison of $J_{13_{\text{CCCH}}}$ with $J_{13_{\text{CH}}}$. In the light of what has been discussed it is reasonable to expect that changes on the ^{13}C will affect $J_{13_{\text{CCCH}}}$ and $J_{13_{\text{CH}}}$ differently. Fig. 3 bears out this expectation. Notice that for para-substituted neopentyl benzoates -- where contributions of factors other than electronegativity are kept constant -- $J_{13_{\text{CCCH}}}$ and $J_{13_{\text{CH}}}$ vary

linearly with each other.

Experimental

Synthesis of Labeled Compounds. All ^{13}C -labeled compounds were prepared by conventional synthetic techniques. Trimethylacetic-1- ^{13}C acid and di-t-butyl ketone-carbonyl- ^{13}C , prepared from the carbonation of t-butyl lithium with carbon dioxide- ^{13}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 C00-1189-16.