only 53 c./sec., for the collapse of which H_2 = 20 milligauss is entirely adequate.

For the exact measurement of changes in irradiation frequency, an EC-60 Counter Adapter,[10] which produces an easily-countable beat frequency by means of a standard crystal, was employed. A BC-221-J frequency meter (Zenith Radio Corp.) was used to establish the direction of increase.

Dichlorofluoromethane was obtained from the Matheson Co.; its doublet fluorine resonance, centered at +80.881 ϕ^*, ± 0.003[8] (5 vol. % in CCl_3F, 0.5% Me_4Si, 24.5°) had J(HF) = 53.65 ± 0.16 c./sec. In the proton spectrum of this solution the doublet center is at 2.587 τ, ± 0.002. The neat liquid, in a 4 mm. i.d. thin-walled tube, was required for the study of the C^{13} compound at natural abundance. The fluorine isotope shift[9] due to C^{13}, $\Delta\phi(C^{13}F)-(C^{12}F)$, was found to be +0.156 ± 0.003 p.p.m., and that for H, +0.004 ± 0.001_5 p.p.m.; while $J(C^{13}F)$ = 293.8 ± 0.2 c./sec., and $J(C^{13}H)$ = 220.0_0 ± 0.1_3 c./sec.

Though three dissimilar nuclei are employed here, the spin decoupling procedure and the interpretation as to relative signs are essentially the same as in the case previously described.[6] Upon irradiation of the low-field (high frequency) C^{13} satellite doublet in the proton spectrum, the high-field C^{13} doublet in the fluorine spectrum drew together. When the irradiation frequency was lowered by about 512 c./sec., the low-field C^{13}–F doublet narrowed instead. Had the coupling constants been of like sign, it would have been necessary to *raise* the irradiation frequency by about 75 c./sec. to achieve this result. Analogous observations were made for H{F} decoupling, further confirming the assignment of unlike signs for $J(C^{13}F)$ and $J(C^{13}H)$.

I thank Emmett B. Aus for the careful n.m.r. spectral work reported here.

CONTRIBUTION NO. 242 FROM THE
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NON-ADDITIVE SUBSTITUENT EFFECTS ON C^{13}-PROTON SPIN-SPIN COUPLINGS[1]

Sir:

It has been reported[2] that C^{13}-proton couplings in the nuclear magnetic resonance spectra of substituted methanes conform to "a simple, but precise, additivity relation." In the belief that a further experimental test of this generalization was desirable, we have measured coupling constants for a number of compounds not previously studied. The results, presented in Table I together with coupling constants calculated using zeta-values,[2] show that the additivity relation is not generally valid.

The accompanying figure is a plot of J_{CH} against n for the two series $CH_{(4-n)}X_n$ in which X is either F or OCH_3. Clearly, the points are not colinear as would be required by the additivity relation. If the data[3] for $CH_{(4-n)}Cl_n$ are similarly plotted, the deviations from colinearity, though smaller, also exceed the experimental error. J_{CH} is usually determined with an uncertainty not exceeding ±1 c.p.s. from proton spectra, although values derived from C^{13} spectra[4,5] may be subject to larger errors.

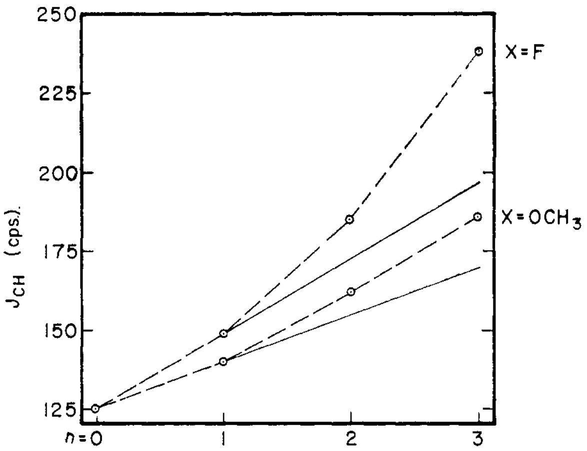

Fig. 1.—J_{CH} as a function of n for two series $CH_{(4-n)}X_n$. If the substituent effects were additive, the points for n = 2 and n = 3 should fall on the extrapolated lines through those for n = 0 and n = 1, shown as solid lines in the figure.

TABLE I

COMPARISON OF MEASURED COUPLING CONSTANTS AND PREDICTIONS BASED ON ZETA VALUES

Compound	J_{CH} (c.p.s.) Observed	Predicted	Difference
$C_6H_5\mathit{CH}_2F$	151[a]	150	+ 1
CH_2F_2	185[b]	173	+12
CHF_3	238	197	+41
$CHFCl_2$	220	203	+17
CHF_2Cl	231	200	+31
$CH_2(COOH)_2$	132[b]	136	− 4
$CH_2ClCOOH$	152	157	− 5
$CHCl_2COOH$	181	184	− 3
CH_3OCH_3	140	[140][c]	[0]
$\mathit{CH}_2(OCH_3)_2$	162	155	+ 7
$\mathit{CH}(OCH_3)_3$	186	170	+16

[a] D. T. Carr, Thesis, Purdue University, 1962. [b] Reference 8. [c] Used to evaluate zeta for the methoxy group as 56.6 c.p.s.

It is not clear how the inadequacy of the proposed additivity relation may affect the problem of interpreting these coupling constants. J_{CH} is believed[3,6–8] to depend primarily on the *s*-character of the carbon atomic orbital used in the C–H bond. It is not known whether this bonding parameter will vary linearly as additional substituents are introduced. Moreover, all theoretical discussions of the dependence of J_{CH} on hybridization have included a number of simplifying assumptions which may not be generally valid. In this connection, it is noteworthy that the largest deviations from the additivity relation occur when one or

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(1) Supported by a grant from the National Science Foundation.

(2) E. R. Malinowski, *J. Am. Chem. Soc.*, **83**, 4479 (1961).

(3) N. Muller and D. E. Pritchard, *J. Chem. Phys.*, **31**, 768, 1471 (1959).

(4) P. C. Lauterbur, *ibid.*, **26**, 217 (1957).

(5) H. Spiesecke and W. G. Schneider, *ibid.*, **35**, 726 (1961).

(6) J. N. Shoolery, *ibid.*, **31**, 1427 (1959).

(7) M. Karplus, *J. Phys. Chem.*, **64**, 1793 (1960).

(8) N. Muller, *J. Chem. Phys.*, **36**, 359 (1962).

more substituent atoms attached to the central carbon are highly electronegative ones.

The experimental procedures used in this work were similar to those previously described.[3]

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SYNTHESIS OF A BORON-LABELED TETRABORANE[1]

Sir:

We wish to report the first synthesis of a boron hydride molecule containing a boron isotopic label *in a specific position.* Skeletal labeled boron hydrides promise to be of considerably greater use in the study of mechanisms of reactions than the deuterium labeled materials that have thus far been produced, since the probability of spontaneous rearrangement without skeletal disruption is much lower.

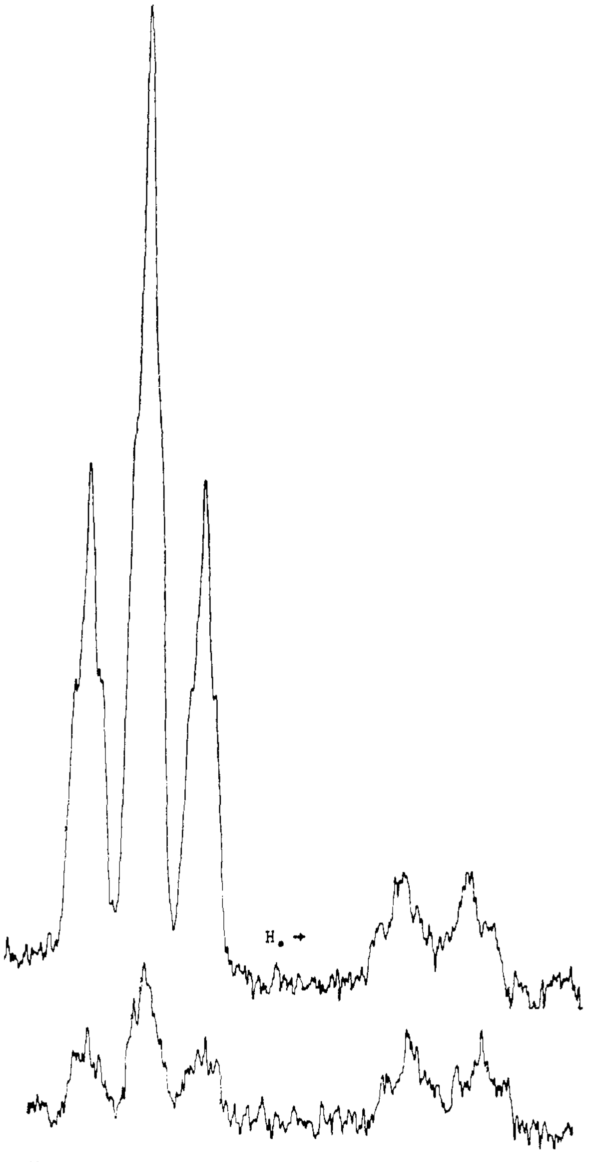

Fig. 1.—^{11}B n.m.r. spectra of tetraboranes: upper trace, ^{11}B enrichment in the 4-position; lower trace, 4% ^{11}B in all positions.

Diborane-^{10}B was prepared by reaction of lithium aluminum hydride with boron trifluoride containing 96% ^{10}B purchased from Oak Ridge National Laboratory. Sodium triborohydride was prepared from the ^{10}B-enriched diborane by reaction with sodium amalgam in diethyl ether.[2] Following isolation and purification by the usual procedure the labeled triborohydride was allowed to react with a mixture of isotopically normal diborane and hydrogen chloride. In a typical reaction 5.39 mmoles of triborohydride was treated for 20 min. at 0° with a mixture of 5.58 mmoles of hydrogen chloride and 5.81 mmoles of diborane. Fractionation of the resulting gaseous mixture by standard techniques resulted in isolation of 2.05 mmoles of tetraborane (−45.2° V.T., 37.5 mm.; lit., interpolated, 37.5 mm.) as well as 5.76 mmoles of diborane and small quantities of hydrogen chloride and higher boranes, including decaborane, $B_{10}H_{14}$. The ^{11}B n.m.r. spectrum of the tetraborane was obtained with a Varian Model 4300B high resolution spectrometer operating at 19.3 Mc./s. and is compared in Fig. 1 with the spectrum of tetraborane-per-96% ^{10}B prepared by the same procedure from diborane-96% ^{10}B and sodium triborohydride-96% ^{10}B. The high field doublet arising from the two B–H groups in the 1,3 positions[3] is of closely comparable intensity in the two spectra (taken under identical instrumental conditions) but the triplet arising from the 2,4 BH_2 positions is considerably more intense in the sample prepared from isotopically normal diborane. Clearly, the ^{10}B is contained in the 4 position almost exclusively except for the four per cent unavoidably introduced into all other positions from the sodium triborohydride.

It has been suggested previously[4] that the pyrolytic conversion of diborane to tetraborane proceeds by formation of triborane-9, conversion of this intermediate to triborane-7 in the rate limiting step, and reaction of triborane-7 with diborane to form tetraborane. We suggest that the present reaction proceeds by the pathway

$$\mathrm{Na^{10}B_3H_8 + HCl \longrightarrow NaCl + {}^{10}B_3H_9} \quad (1)$$

$$\mathrm{3/2\,{}^{10}B_2H_6 \longleftarrow {}^{10}B_3H_9 \longrightarrow {}^{10}B_3H_7 + H_2} \quad (2)$$

$$\mathrm{{}^{10}B_3H_7 + {}^{11}B_2H_6 \longrightarrow {}^{10}B_3{}^{11}BH_{10} + {}^{11}BH_3} \quad (3)$$

Mass spectrometric analysis of the selectively labeled sample showed that it contained about 16% ^{11}B. Assuming that the 1, 2 and 3 positions contain only 4% ^{11}B coming from the triborohydride, the 4 position is estimated to contain 52% ^{11}B. Less than complete ^{11}B labeling in the 4 position arises from two principal causes.

(a) Since isotopically normal diborane used as the source of ^{11}B contains 20% ^{10}B, the lighter iso-

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(1) Interconversion of Boranes. V. For paper IV of this series see G. L. Brennan and R. Schaeffer, *J. Inorg. Nucl. Chem.*, **20**, 205 (1961).

(2) W. V. Hough, L. J. Edwards and A. D. McElroy, *J. Am. Chem. Soc.*, **80**, 1828 (1958).

(3) For the numbering system recommended for boron compounds see the Preliminary Report of the Advisory Committee on the Nomenclature of Organic Boron Compounds, available through *Chemical Abstracts*.

(4) R. E. Enrione and R. Schaeffer, *J. Inorg. Nucl. Chem.*, **18**, 103 (1961).