Nuclear Magnetic Resonance Spectroscopy. Carbon–Carbon Coupling[1a]

Frank J. Weigert[1b] and John D. Roberts*

Contribution No. 4320 from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California 91109.

Received August 26, 1971

Abstract: One-bond, carbon–carbon coupling constants have been observed for several series of compounds containing ^{13}C in its natural abundance of 1.1% at both sites. The small (10–15 Hz) coupling constants in cyclopropanes show that the carbon–carbon bonds have low s character. Substituent and hybridization effects on the carbon–carbon coupling of aliphatic and alicyclic alcohols, ketones, and five- and six-membered aromatic heterocycles have been observed. Carbon–carbon couplings in methyl derivatives are proportional to carbon–proton coupling in similar bonding situations, with a slope similar to that predicted and observed by Karabatsos for the correlation of carbon–proton and proton–proton couplings. Two- and three-bond carbon–carbon coupling constants are interpreted in terms of the Fermi contact mechanism by correlations with proton–proton and carbon–proton coupling constants in similar bonding situations.

Carbon–carbon coupling constants have not been very extensively studied because the difficulties of even observing a ^{13}C resonance are greatly compounded by the necessity of having to obtain spectra of compounds containing two ^{13}C atoms. A number of studies of carbon–carbon coupling[2,3] have been made using doubly labeled compounds, but the symmetry of the spin systems allowed most of the desired information to be obtained from the proton spectra. These were complicated because the materials studied were mixtures of doubly labeled, singly labeled, and unlabeled species. Frei and Bernstein[4] observed carbon–carbon couplings in the ^{13}C spectra of doubly labeled compounds without proton decoupling. They found that the magnitudes of the carbon–carbon couplings were related to the product of the s characters of the two orbitals forming the carbon–carbon bond.

With improved instrumentation, carbon–carbon couplings were later studied with single labeled substances, either by direct observation[5] or by heteronuclear tickling.[6] The signs of one-bond carbon–carbon couplings are the same as one-bond carbon–proton couplings by heteronuclear double resonance[5,6] and vicinal proton–proton couplings by detailed analysis of second-order spectra.[2,3]

Carbon–carbon couplings can now be observed with molecules containing ^{13}C in its natural abundance of 1.1% at each site[7,8] using time averaging, field-frequency stabilization, and complete proton decoupling. A number of carbon–carbon couplings measured this way are reported here.

Experimental Section

Unless otherwise mentioned, compounds used in this work were obtained from commercial sources or were available from previous studies. Propyne labeled with 53% ^{13}C at C-3 was kindly provided by Dr. J. N. Shoolery. Methylcyclopropane labeled with 20% ^{13}C at the methyl carbon was prepared previously.[9] Spectra were obtained in the external lock mode of the Varian DFS-60 spectrometer with complete proton decoupling. A good description of the procedure has been given by Litchman and Grant for the AFS-60 spectrometer system.[8] Because of field instabilities, several sets of intermediate spectra were punched on cards using the Varian C-1001 interface unit and the digitized spectra were later processed on an IBM 7094 computer. The precision of the coupling constants is approximately ±2%; because concentration and solvent effects have not been considered, accuracy is unknown.

Results

The extremely low signal-to-noise ratios for the ^{13}C satellites of the ^{13}C spectrum (at best 0.2/1 for a single scan) necessitated some care in verifying the reality of a supposed ^{13}C satellite peak. The ideal arrangement, ^{13}C homonuclear tickling with simultaneous, complete proton decoupling, was not practical because of the weakness of the natural-abundance carbon signals, and because the modulation and sweep systems of the DFS-60 do not lend themselves well to homonuclear decoupling experiments. Spinning side bands do not cause the satellites because the line positions were unaffected by changes in spinning rate and they were not symmetrically located about the intense peak of the singly labeled materials. When the spacings of the peaks in the ^{13}C satellite spectra were used to calculate δ_{AB}, the values so obtained agreed well, neglecting isotope effects, with δ_{AB} for the resonances of the singly labeled species. This agreement is additional evidence that the identification of the satellite is correct.

Anderson and Freeman[10] have shown that the X part of an $A_iB_j \cdots X$ system can be collapsed to a single line by a strong enough decoupling field. Because the ^{13}C spectrum of a single labeled species is the X part

---

[1] (a) Supported by the National Science Foundation, and the Public Health Service, Research Grant No. GM11072 from the Division of General Medical Sciences. (b) National Science Foundation Predoctoral Fellow, 1965–1968.

[2] R. M. Lynden-Bell and N. Sheppard, *Proc. Royal Soc., Ser. A*, **269**, 385 (1962).

[3] (a) D. M. Graham and C. E. Holloway, *Can. J. Chem.*, **41**, 2114 (1963), and private communication from R. M. Lynden-Bell quoted therein; see also R. E. Carhart and J. D. Roberts, *Org. Magn. Resonance*, 3, 139 (1971); A. S. Perlin and B. Casu, *Tetrahedron Lett.*, 2921 (1969); H. Dreeskamp, K. Hildenbard, and G. Pfisterrer, *Mol. Phys.*, 17, 429 (1969); (b) G. A. Gray, G. E. Maciel, and P. D. Ellis, *J. Magn. Resonance*, 1, 407 (1969); G. A. Gray, P. D. Ellis, D. D. Traficante, and G. E. Maciel, *ibid.*, 2, 41 (1969); G. E. Maciel, P. D. Ellis, J. J. Natterstad, and G. B. Savitsky, *ibid.*, 1, 589 (1969).

[4] K. Frei and H. J. Bernstein, *J. Chem. Phys.*, 38, 1216 (1963).

[5] D. M. Grant, *J. Amer. Chem. Soc.*, **89**, 228 (1967).

[6] K. A. McLauchlan, *Chem. Commun.*, 105 (1965).

[7] F. J. Weigert and J. D. Roberts, *J. Amer. Chem. Soc.*, **89**, 5962 (1967).

[8] W. M. Litchman and D. M. Grant, *ibid.*, **89**, 6775 (1967).

[9] E. Renk, P. R. Shafer, W. H. Graham, R. H. Mazur, and J. D. Roberts, *ibid.*, **83**, 1987 (1961).

[10] W. A. Anderson and R. Freeman, *J. Chem. Phys.*, 37, 85 (1962).

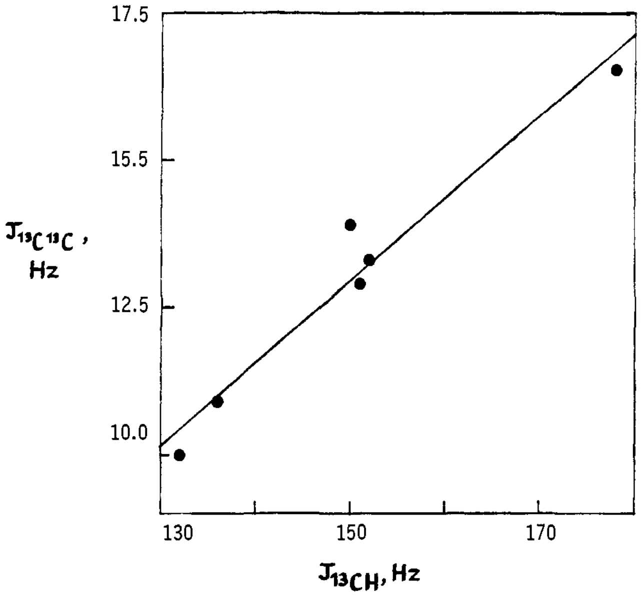


Figure 1. Correlation between $J_{^{13}C-^{13}C}$ for 1,2 bonds of cyclopropane derivatives of the type $(CH_2)_2CXY$ and $J_{^{13}C-H}$ for methane derivatives of the type CH_2XY.

of an $A_iB_j \cdots X$ spin system, a single line is expected to result under the decoupling conditions used in our experiments. Any remaining resonances must then be due to multiply labeled species or impurities.

The possibility of impurities in low concentrations comparable to the doubly labeled species which provide the ^{13}C satellites is difficult to eliminate, but the probability that impurities would be present in just the correct concentrations and have just the right ^{13}C and proton chemical shifts to simulate carbon–carbon coupling constants seems small.

A preliminary account of carbon–carbon coupling constants in cyclopropanes has been presented.[7] The reported and some further carbon–carbon coupling constants of substituted cyclopropanes are given in Table I. Litchman and Grant[8] found small, but significant, substituent effects on the carbon–carbon coupling constants in *tert*-butyl derivatives. Similar variations are seen in cyclopropane derivatives. The carbon–carbon couplings in substituted cyclopropanes are proportional to the carbon–proton couplings in substituted methanes, as shown in Figure 1. Because the coupling constants increase with substituent electronegativity, the compounds in which the first atom of a substituent is carbon, such as dicyclopropyl ketone or cyclopropanecarboxylic acid, provide the closest models to cyclopropane itself. Thus, the carbon–carbon coupling in cyclopropane is expected to be approximately 10 Hz. The magnitudes of the substituent effects on carbon–carbon coupling constants are quite similar in the cyclopropanes and the *tert*-butyl derivatives.[8]

Table I. Carbon–Carbon Coupling Constants in Cyclopropane Derivatives

Compound	Bond	$^1J_{CC}$, Hz
Cyclopropanecarboxylic acid	1,2	10.05
	1,α	72.5
Dicyclopropyl ketone	1,2	10.2
	1,α	54.0
Cyclopropyl cyanide	1,2	10.9
	1,α	77.9
Methylcyclopropane	1,α	44.0
Cyclopropyl iodide	1,2	12.9
Cyclopropyl bromide	1,2	13.3
Cyclopropyl chloride	1,2	13.9
1,1-Dichlorocyclopropane	1,2	16.55

One-bond, carbon–carbon coupling constants of some aliphatic and alicyclic compounds are given in Tables II and III. Estimating a bromine substituent effect and assuming that the substituent effect on a β,γ bond is negligible gives an extrapolated value for the carbon–carbon coupling in cyclobutane of 27 Hz.

Table II. One-Bond, Carbon–Carbon Coupling Constants in Aliphatic Compounds

Compound	Bond	$^1J_{CC}$, Hz
Ethanol	1,2	37.7
2-Propanol	1,2	38.4
2-Methyl-2-propanol	1,2	39.5[a]
1-Propanol	1,2	37.8
	2,3	34.2
3-Pentanol	1,2	35.0
	2,3	37.9
Acetone	1,2	40.6
3-Pentanone	1,2	35.7
	2,3	39.7
Propyne	2,3	67.4
Dimethyl acetylenedicarboxylate	C-CO	123

[a] Reference 8.

Table III. One-Bond, Carbon–Carbon Coupling Constants in Alicyclic Systems

Compound	Bond	$^1J_{CC}$, Hz
Bromocyclobutane	1,2	29.6
	2,3	27.1
Cyclobutanone	1,2	29.7
	2,3	28.5
Cyclopentanone	1,2	37.2
	2,3	34.4
Cyclohexanone	1,2	37.3
Cyclopentanol	1,2	36.0
	2,3	32.6
Cyclohexanol	1,2	35.8
Tetrahydrofuran	2,3	33.0

The coupling constant to the carbonyl carbon in cyclohexanone is simlar to the corresponding one in cyclopentanone. Cyclobutanone, on the other hand, has significantly smaller carbon–carbon coupling constants which suggests the bonding orbitals rehybridize due to ring strain. The β,γ coupling constant in cyclobutanone differs from that in bromocyclobutane, perhaps because of the difference between a planar ketone and a puckered bromide. The coupling constants to the carbinyl carbon in cyclohexanol and cyclopentanol are also similar which again suggests that there is no great angle strain in either the five- or six-membered rings.

The carbon–carbon coupling constant in ethanol is 3.1 Hz larger than that in ethane. Substituting a methyl group on the β carbon to form 1-propanol does not significantly alter the value of the coupling constant between the α and β carbons. The β,γ coupling in 1-propanol does not differ greatly from that in ethane.

However, substituting a methyl at the α position of ethanol to give 2-propanol increases $^1J_{CC}$. The same effect occurs when a second methyl is added to form 2-methyl-2-propanol.[8] The coupling in cyclic alcohols is significantly smaller than the corresponding alicyclic compounds.

The only carbon–carbon coupling constant where both carbons are in an aromatic ring was obtained by Bernstein[11] who measured the 57.0-Hz carbon–carbon coupling in benzene itself. Ethylene has a J_{CC} of 67.6 Hz.[2,3a] The coupling constants we have observed for some unsaturated compounds are given in Table IV.

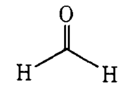
Table IV. One-Bond, Carbon–Carbon Coupling Constants in Unsaturated Systems

Compound	$^1J_{C\text{-}1-C\text{-}2}$	$^1J_{C\text{-}2-C\text{-}3}$	$^1J_{C\text{-}3-C\text{-}4}$
Aromatic Compounds			
Benzene	57.0[a]		
Pyridine		53.8	53.5
Nitrobenzene	55.4	56.3	55.8
Iodobenzene	60.4	53.4	58.0[c]
Anisole		58.2	56.0
Aniline	61.3	58.1	56.2
Pyrrole		65.6	
Furan		69.1	
Thiophene		64.2[c]	
Alkenic Compounds			
Ethylene[b]	67.6		
1,1-Dimethylallene		99.5	
Acrylonitrile	70.6		
Acrylic acid	70.4 (1,α)		

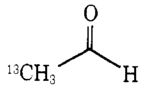
[a] Reference 11. [b] References 2 and 3a. [c] Only the inner two lines of the AB pattern were observed.

Furan, pyrrole, and thiophene all have carbon–carbon coupling constants similar to that of ethylene, while in the six-membered aromatic ring compounds the couplings are similar to that of benzene. The accuracy of these couplings is lower than for the cyclopropane couplings because wider sweep ranges were necessary. The substituent effects are rather more erratic than those observed for the aliphatic compounds and could well represent subtle changes in the σ bonding, as well as π-electron effects.

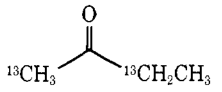
Formaldehyde has a large proton–proton coupling constant,[12] and aldehydes have large two-bond carbon–proton coupling constants.[13] If carbon–carbon coupling is dominated by similar mechanisms, the geminal, cross-carbonyl, carbon–carbon coupling in ketones should be large. The two-bond, carbon–carbon coupling of 2-butanone is 15.2 Hz.[2] Large geminal carbon–proton coupling constants which have no analogy in proton–proton coupling occur in acetylenes.[2,3,14] The geminal carbon–carbon coupling in propyne is 11.8 Hz.



$^2J_{HH} = 40$ Hz



$^2J_{CH} = 26$ Hz



$^2J_{CC} = 15.2$ Hz

Besides the satellites due to the one-bond coupling, inner satellites are symmetrically located about the α and β carbon resonances of pyridine but no satellites of similar magnitude flank the γ carbon. The peaks which correspond to the vicinal carbon–carbon coupling constant of 13.95 Hz in pyridine are shown in Figure 2. Similar, though smaller, couplings were observed in some spectra of substituted benzenes. Long-range carbon–carbon coupling constants are given in Table V.

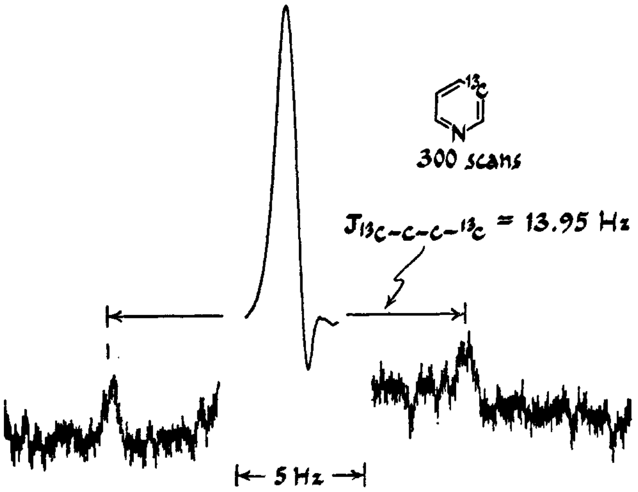


Figure 2. Proton-decoupled cmr spectrum of the β carbon of pyridine showing the satellites arising from the coupling to the remote α carbon.

Table V. Longer Range Carbon–Carbon Coupling Constants

Compound	Carbons	$^2J_{CCC}$, Hz
Two-Bond		
Propyne	1,3	11.8
2-Butanone	1,3	15.2
Cyclobutanone	1,3	9.5
Bromocyclobutane	1,3	9.0
Three-Bond		
		$^3J_{CCCC}$
Pyridine	2,5	13.95
Aniline	2,5	7.9
Iodobenzene	2,5	8.6
Nitrobenzene	2,5	7.6

Discussion

In the average energy approximation for calculation of coupling constants,[15] if the coefficients of the wave functions of two compounds are identical, then two coupling constants, for example, carbon–proton and proton–proton, may be related by

$$J_{CH} = \left(\frac{\gamma_C}{\gamma_H}\right)\left(\frac{\phi\,^{13}C(0)}{\phi\,^{1}H(0)}\right)\left(\frac{\Delta E_H}{\Delta E_C}\right)J_{HH} \tag{1}$$

where $\phi(0)$ is the electron density at the nucleus. Karabatsos[16] showed that (1) can be simplified further to

$$J_{CH} = aJ_{HH} \tag{2}$$

where a varies with the hybridization of the carbon, and for sp^3, $a = 0.3$, for sp^2, $a = 0.4$, and for sp, $a = 0.6$.

---

(11) H. J. Bernstein, private communication.

(12) B. L. Shapiro, R. M. Kopchik, and S. J. Ebersole, *J. Chem. Phys.*, **39**, 3154 (1963).

(13) E. Sackmann and H. Dreeskamp, *Spectrochim. Acta*, **21**, 2005 (1965).

(14) M. P. Simonnin, *Bull. Soc. Chim. Fr.*, 1774 (1966).

(15) J. A. Pople and D. P. Santry, *Mol. Phys.*, **8**, 1 (1964).

(16) G. J. Karabatsos, J. D. Graham, and F. M. Vane, *J. Amer. Chem. Soc.*, **84**, 37 (1962).

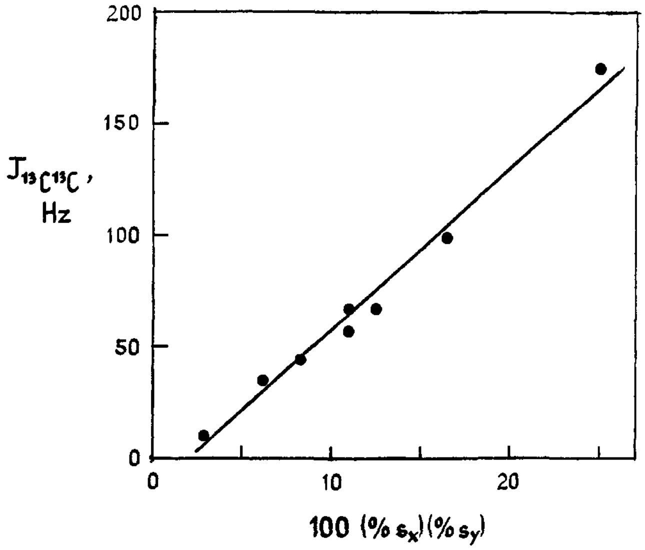


Figure 3. Correlation between $J_{^{13}C-^{13}C}$ and the degree of s character of the C–C bond as defined by the total s character of the orbitals of the carbon (s_x) contributing to one end of the bond times the s character of the orbitals of the carbon (s_y) contributing to the other end of the bond times 100. For allene, s_x of C-1 is 33% (sp^2 carbon–carbon bond) and s_y of C-2 is 50% (sp carbon–carbon bond) so that $(s_xs_y)100 = 16.5$.

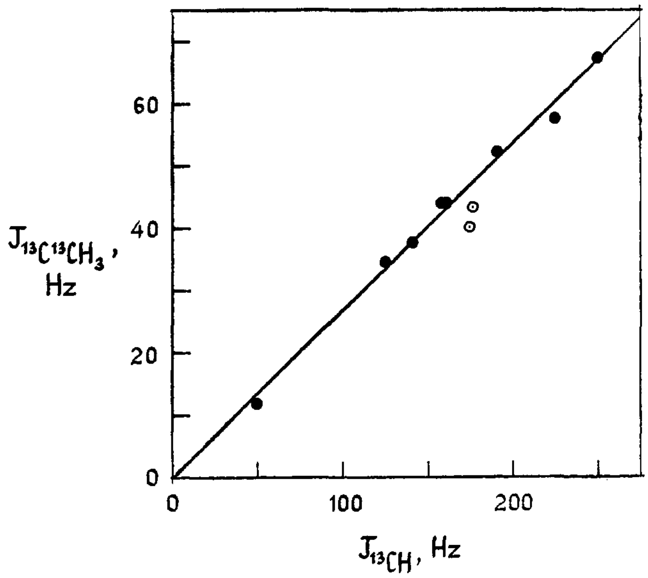


Figure 4. Correlation between $J_{^{13}CH}$ in compounds of the type $XYZ^{13}CH$ and $J_{^{13}C^{13}C}$ in compounds of the type $XYZ^{13}C^{13}CH_3$ (filled circles). The open circles show the results for benzaldehyde-acetophenone and acetaldehyde–acetone which were not used in the least-squares fit for the correlation line.

The carbon orbitals used in forming the carbon–proton bonds of cyclopropane have 33% s character on the basis of carbon–proton coupling constants.[17,18] Such correlations of carbon–proton coupling with carbon orbital hybridization seem valid in hydrocarbons.[19]

Foote[20] and Lippert and Prigger[21] in studies of carbon–proton coupling in cycloalkanes have suggested that because the carbon orbitals forming the carbon–proton bonds have more s character than normal hydrocarbons, the orbitals forming the carbon–carbon bonds must have more p character. If each carbon uses a single 2s orbital to form all of its bonds,[22] and the two exocyclic orbitals have 33% s character each, then 34% s character is left to be divided between the two endocyclic orbitals, *i.e.*, 17% s character each. This is roughly sp^5 hybridization.[23]

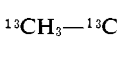
Assuming that changes in carbon–carbon coupling are entirely due to hybridization effects, the predicted carbon–carbon coupling for cyclopropane, using the coupling in ethane as a model for two orbitals with 25% s character, is $(0.17/0.25)^2 \times 34.6 = 16$ Hz. Ten Hz has been extrapolated for the parent compound from consideration of the substituent effects.

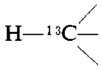
Several possibilities can rationalize this discrepancy. Although there may be a significant contribution to the coupling constant from other than the Fermi contact interaction, the deviation between the simplified calculation and the experimental result is more likely due to the approximations used to evaluate the Fermi contact term.

Figure 3 shows the correlation of carbon–carbon coupling in hydrocarbons with the product of the orbital hybridizations. Ten per cent changes in the effective nuclear charge may be sufficient to explain the fact that the line does not go through the origin. Variations of this magnitude are not unreasonable.[24]

From Figure 3 the hybridization of the endocyclic orbitals in cyclobutane corresponding to a 27-Hz coupling constant, 23% s, is consistent with the 27% s character in the exocyclic orbitals found from studies of the carbon–proton coupling constant.[20,21]

Smith[25] has applied eq 3 to the geminal, metal–proton coupling constants in the tetramethyl derivatives of group IV, and later Weigert, Winokur, and Roberts[26] used the same formalism to relate the one-bond, carbon–metal coupling constants to the carbon–carbon coupling in neopentane. The carbon–carbon coupling in neopentane was also compared with the carbon–proton coupling in methane. This correlation of carbon–carbon and carbon–proton coupling has been extended to other pairs of compounds and is shown in Figure 4. The close agreement between the slope (0.27) of this correlation and the value of 0.3 calculated by Karabatsos for the correlation of carbon–proton and proton–proton coupling and the zero intercept suggests that the coupling mechanisms are similar and, furthermore, the same degree of approximation suffices to explain all three types of coupling.





The same correlation may be extended to other carbon hybridizations, though not as many data are available. Comparisons follow of the carbon–carbon coupling involving the carbonyl carbon of some esters, along

---

(17) J. N. Shoolery, *J. Chem. Phys.*, 31, 1427 (1959).

(18) N. Muller and D. E. Pritchard, *ibid.*, 31, 768 (1959).

(19) *Cf.* D. M. Grant and W. M. Litchman, *J. Amer. Chem. Soc.*, 87, 3994 (1965), for discussion of electronegativity effects in substituted hydrocarbons.

(20) C. S. Foote, *Tetrahedron Lett.*, 579 (1963).

(21) E. Lippert and H. Prigger, *Ber. Bunsenges. Phys. Chem.*, 67, 415 (1963).

(22) C. Juan and H. S. Gutowsky, *J. Chem. Phys.*, 37, 2198 (1962).

(23) W. A. Bernett, *J. Chem. Educ.*, 44, 17 (1967).

(24) D. M. Grant, private communication.

(25) G. W. Smith, *J. Phys. Chem.*, 39, 2031 (1963).

(26) F. J. Weigert, M. Winokur, and J. D. Roberts, *J. Amer. Chem. Soc.*, 90, 1566 (1968).

with the carbon–proton coupling in ethyl formate. Strict application of the Karabatsos proportionality constants yields calculated carbon–carbon coupling constants which are all slightly too large, but the agreement with the experimental values is still good (Chart I).

Chart I

$H\overset{O}{\overset{\|}{C}}OR$		$CH_3\overset{O}{\overset{\|}{C}}OR$	$=C\overset{O}{\overset{\|}{C}}OR$	$\equiv C\overset{O}{\overset{\|}{C}}OR$
$J_{CH} = 226$ Hz	$J_{CC} =$	58.5[a]	76.3[b]	123[b]
	$J_{CC}/J_{CH} =$ (obsd)	0.26	0.34	0.54
	$J_{CC}/J_{CH} =$ (predicted from hybridization alone)	0.3	0.4	0.6

[a] G. E. Maciel, private communication; see also ref 3b. [b] Reference 4.

The variations in carbon–proton coupling are most likely due both to changes in the effective nuclear charge and the hybridization of the carbon orbital;[19] hence, it follows that because of the proportionality between carbon–carbon and carbon–proton coupling, similar changes also affect carbon–carbon coupling, but with reduced magnitudes.

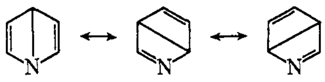
In some cases, however, marked deviations are found. The comparison of carbon–proton coupling in aldehydes with carbon–carbon coupling in ketones, while qualitatively reasonable, deviates significantly from the correlation line of Figure 4. A comparison of the carbon–carbon coupling in acetonitrile with the analogous coupling in propyne is also not as expected for a nitrogen substituent effect. In both cases, the anomaly

$$^{13}CH_3{-}^{13}C{\equiv}N \qquad ^{13}CH_3{}^{13}C{\equiv}CH$$

seems to be associated with shifts in the electronic absorption spectrum, which may be correlated either with changes in the average excitation energy or with the failure of the approximation of eq 2.

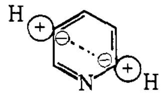
The size of the two-bond coupling in 2-butanone is about as expected by extrapolation of the appropriate two-bond couplings in formaldehyde and acetaldehyde. If the mechanism of this coupling is as suggested, the sign should be positive. The large 1,3-carbon–carbon couplings in the cyclobutanes may reflect the effect of the bond angles on geminal couplings. Proton–proton couplings become more negative as the H–C–H bond angle is reduced, and at 90°, a large negative proton–proton coupling is predicted.[27] If this carbon–carbon coupling involves similar considerations, it should be negative. The geminal carbon–carbon coupling in propyne is predicted to be positive by analogy with the carbon–proton coupling in acetylene. This two-bond coupling involving a methyl carbon fits the correlation line of Figure 4 for one-bond coupling while the two-bond coupling in 2-butanone does not.

There is no good proton–proton or carbon–proton analogy for the carbon–carbon couplings observed in the aromatic compounds. The unusually large magnitudes of these couplings may be because they are doubly vicinal; that is, there are two equivalent paths for the spin information to be transmitted through the σ bonds, and the effects are expected to be additive. In elementary π-valence bond theory, the five canonical structures for pyridine are the three Dewar structures and the two Kekule structures. The Dewar structures **1**



1

imply pairing of the $2p_z$ electrons of the opposite ring carbons. Because p electrons do not contribute directly to the Fermi contact interaction, a σ,π interaction, in which the spin-pairing of the π system is transmitted to the σ electrons, seems necessary to account for any coupling to be ascribed to the pairing schemes **1**. As an alternative, we note that the back lobes of the sp^2 orbitals used in forming the carbon–proton bonds have some 2s character, and perhaps direct electron pairing *via* these orbitals could produce the observed coupling by a "through-space" mechanism as shown by **2**.



2

The two-bond coupling in 2-butanone and the three-bond coupling in pyridine are both larger than the one-bond couplings in some cyclopropanes. This might indicate that there is a greater s bond order between some formally nonbonded carbons than between the directly bonded carbons in cyclopropanes. Correlations of carbon–carbon coupling with s bond order seem, at best, reserved for one-bond coupling constants.

Isotope Effects on the Chemical Shift. Substituting ^{13}C for ^{12}C shifts a directly bonded fluorine upfield *ca.* 0.1 ppm. Even through two bonds, an isotope effect of 0.01 ppm is observable.[28] The isotope effect of ^{13}C on another ^{13}C resonance has been reported to be 0.3 ppm upfield in ethylene.[3] Because this was the result of the analysis of five- and six-spin systems, errors could be this large. In this study, simple AB spectra were obtained which did not require complicated calculations to obtain the isotope shifts. Those observed were small, and in most cases were within the experimental error of the measurement. Both carbons in thiophene are shifted upfield by 0.03 ppm and the AB spectrum of C-1 and C-2 of 3-pentanol was shifted 0.01 ppm upfield relative to the species with only one ^{13}C.

Acknowledgment. We would like to thank Professors D. M. Grant and G. E. Maciel for providing data on their measurements of carbon–carbon coupling constants prior to publication.

---

(27) J. A. Pople and A. A. Bothner-By, *J. Chem. Phys.*, **42**, 1339 (1965).

(28) N. Muller and D. T. Carr, *J. Phys. Chem.*, **67**, 112 (1963).