Conformational and Substituent Dependencies of $^{13}C-^{13}C$ Coupling Constants

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Abstract: Experimentally determined ^{13}C chemical shifts and $^{13}C-^{13}C$ coupling constants are reported for a series of aliphatic and alicyclic alcohols containing ^{13}C-labeled methyl groups. Results for $^{13}C-^{13}C$ coupling constants over one, two, and three bonds are compared with theoretical results for 2-butanol. The calculated values are based on the finite perturbation formulation in the INDO (intermediate neglect of differential overlap) approximation of self-consistent-field molecular orbital (SCF-MO) theory. Best agreement is found for vicinal $^{13}C-^{13}C$ coupling constants, which exhibit a strong dependence on the dihedral angle measured about the C2-C3 bond. In contrast to vicinal H-H coupling and $^{13}C-^{13}C$ coupling in a series of ^{13}C-labeled carboxylic acids, the cis coupling is larger than the trans vicinal coupling constant. This effect is probably general and can be attributed to the interactions between the orbitals on the C_1 and C_4 carbon atoms in the cis arrangement.

Directly bonded, geminal, and vicinal $^{13}C-^{13}C$ coupling constants exhibit dependencies on conformations, substituents, and hybridization effects. However, the large fractional changes, which are observed for this type of vicinal coupling, should make these useful for studies of molecular conformation in solution. The angular dependence of vicinal H-C-C-H[2-3] and other types of vicinal[4-7] coupling constants can usually be represented by a functional relationship of the form

$$^3J_{NN'} = A \cos^2 \phi + B \cos \phi + C \qquad (1)$$

where ϕ is the dihedral angle measured from the plane in which the two bonds containing the coupled nuclei (N and N′) are eclipsed. It has been shown that this trigonometric form is to be expected[8] when the dominant interaction occurs between the vicinal hybrid orbitals, which are directed toward the coupled atoms. In the case of vicinal H-H coupling the constant B in eq 1 is negative in sign, so that the trans coupling ($\phi = 180°$) is greater than the cis coupling constant ($\phi = 0°$). Since C in eq 1 has the smallest magnitude of the three constants, vicinal H-H coupling constants nearly vanish for dihedral angles near 90°.

The physical situation presented by vicinal $^{13}C-^{13}C$ coupling is more complicated than H-H coupling because of the greater number of possibilities for substitution and other effects at the two carbon atoms. The experimental and theoretical results for $^3J_{CC'}$, which are presented here, show that the trans coupling is less than the cis coupling, and that an expression of the form of eq 1 does not, in general, provide an adequate representation of the conformational dependence. Furthermore, it will be necessary to sort out the effects of substituents as these can have a very large effect on the $^{13}C-^{13}C$ coupling constants.

The directly bonded and geminal $^{13}C-^{13}C$ coupling constants, which were also observed, show relatively small changes due to conformational effects. Indeed, for these types of coupling constants the correlation with the theoretical results is insubstantial and does not permit any conclusions to be drawn.

Experimental Section

The enriched alcohols were prepared via Grignard reactions between 1 mol of the appropriate ketone and 1 mol of ^{13}C-enriched (67%) methylmagnesium iodide using standard procedures: 2-methyl-2-butanol (**1**).[9] 50:50 mixture of *cis*- and *trans*-4-*tert*-butyl-1-methylcyclohexanols[9] (**2** and **3**). *exo*-2-methyl-2-norbornanol[10] (**4**). and *exo*-2-methyl-2-fenchol[11] (**5**). Reactions of this type which are carried out without excess labeled methyl iodide lead to alcohols contaminated with ketones. The ^{13}C spectra were recorded as the mixture and no overlap of peaks was encountered in extraction of the coupling constant data.

Spectral assignments were made by off-resonance decoupling techniques[12,13] and comparisons with chemical shift data for model compounds.[13-15]

Coupling constant data for **1** were obtained in the Fourier transform mode on a Bruker Scientific WH-90 Fourier transform NMR spectrometer operating at a frequency of 22.64 MHz. The values in Table I are averages of values obtained with spectral widths of 300-1200 Hz. Experimental data for **2-5** were obtained in the continuous wave mode on a Varian Associates XL-100 NMR spectrometer operating at a frequency of 25.14 MHz, and sweep widths of 25 and 50 Hz. Because the compounds were only about 67% enriched in ^{13}C, singlets of about the same intensity due to the unlabeled material appeared between the spin-coupled doublets. As a consequence, this placed a limit on the smallest coupling constants which could be resolved. Errors in the reported coupling constants are estimated to be less than 0.2 Hz.

Theoretical Calculations of $^{13}C-^{13}C$ Coupling Constants in Model Compounds

Molecular orbital (MO) calculations of $^{13}C-^{13}C$ coupling constants for several model compounds were based on the finite perturbation theory (FPT) formulation[16] in the INDO (intermediate neglect of differential overlap) approximation[17,18] of self-consistent-field (SCF) MO theory. This method, which includes all valence electrons in the basis set, has been quite useful for calculating molecular properties such as geometries, dipole moments, hyperfine and nuclear spin-spin coupling constants.

Bond distances and bond angles were based on the standard geometrical model.[19] However, coordinates for the carbonyl group in the calculations for butanoic acid were based on coordinates from the compilation of Sutton.[20] In 2-butanol the OH orientation was assumed to be trans to the C2-H bond. Since the C2 carbon atom is an asymmetric center, for the (R)- and (S)-2-butanol the dihedral angle ϕ is measured clockwise and counterclockwise, respectively, as one looks down the C2-C3 bond axis. This situation is depicted diagrammatically for several values of the dihedral angle in Figure 1.

The calculated values of the $^{13}C-^{13}C$ coupling constants from the C1 carbon atom to the other three carbon atoms and the total energies in atomic units are entered in Table I for 15° intervals of the dihedral angle ϕ. Another calculation was performed at 5° to investigate the possibility that there might be a shift in the maximum vicinal coupling from the 0° value. The INDO energies are given in the last column of Table I. These values are given relative to the

Table I. Calculated INDO–FPT Results for C–C Coupling Over One, Two, and Three Bonds in 2-Butanol as a Function of Dihedral Angle ϕ

Dihedral Angle ϕ, deg	^1J (Cl–C2),[a] Hz	^2J (Cl–C3),[a] Hz	^3J (Cl–C4),[a] Hz	Energy,[b] au × 10^3
0	53.24	−3.93	5.34	7.45
5	53.20	−3.93	5.30	7.20
15	52.93	−3.94	4.81	5.67
30	52.21	−3.99	3.79	3.23
45	51.30	−4.05	2.93	1.73
60	50.36	−4.16	1.97	0.41
75	49.55	−4.33	1.02	0.00[b]
90	49.01	−4.53	0.50	0.57
105	48.69	−4.69	0.55	1.67
120	48.46	−4.72	1.10	2.71
135	48.25	−4.62	1.93	2.54
150	48.01	−4.45	2.77	1.28
165	47.74	−4.31	3.44	0.16
180	47.49	−4.25	3.82	0.07
195	47.32	−4.28	3.79	1.14
210	47.28	−4.41	3.31	2.75
225	47.38	−4.56	2.49	3.97
240	47.63	−4.67	1.57	4.07
255	48.03	−4.66	0.83	3.00
270	48.60	−4.56	0.51	1.40
285	49.36	−4.41	0.77	0.37
300	50.31	−4.27	1.56	0.83
315	51.34	−4.16	2.48	2.22
330	52.27	−4.06	3.40	3.57
345	52.97	−3.98	4.59	5.83

[a] Carbon atoms are labeled as in 1. [b] Energies relative to the minimum value of −52.74983 au, which occurs at ϕ = 75°.

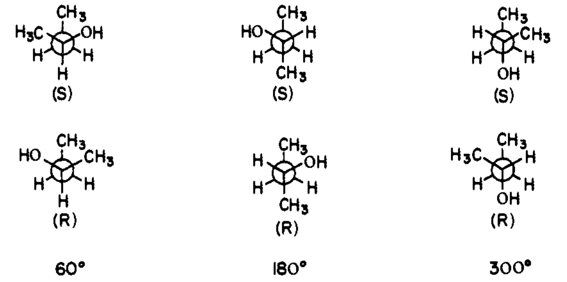


Figure 1. *R* and *S* optical isomers of 2-butanol for dihedral angles of 60, 180, and 300°.

Table II. Calculated INDO–FPT Results for C–C Coupling Constants Over One, Two, and Three Bonds in Butane with Energies in Atomic Units as a Function of the Dihedral Angle ϕ

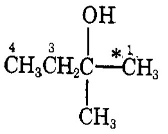
Dihedral Angle ϕ, deg	^1J (Cl–C2), Hz	^2J (Cl–C3), Hz	^3J (Cl–C4) Hz	Energy,[a] au × 10^3
0	46.33	−4.97	5.79	6.25
30	45.48	−5.04	3.96	2.53
60	43.48	−5.21	1.94	0.18
90	42.26	−5.56	0.56	0.63
120	41.30	−5.69	1.45	2.77
150	40.72	−5.39	3.34	1.58
180	40.53	−5.16	4.63	0.00[a]

[a] Energy values are relative to the minimum of −35.16839 au at ϕ = 180°.

Table III. Calculated INDO–FPT Results for C–C Coupling Constants Over One, Two, and Three Bonds in Butanoic Acid with Energies as a Function of Dihedral Angle ϕ

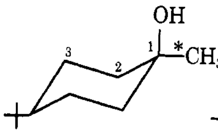
Dihedral Angle ϕ, deg	^1J (Cl–C2), Hz	^2J (Cl–C3), Hz	^3J (Cl–C4), Hz	Energy,[a] au × 10^3
0	82.77	−5.54	1.76	22.41[b]
30	81.80	−6.34	2.27	24.22[b]
60	81.70	−6.30	1.24	0.00[a]
90	79.84	−6.34	0.71	1.00
120	77.74	−6.22	2.14	3.43
150	77.70	−5.85	4.65	1.99
180	78.14	−5.64	5.87	0.11

[a] Energy values relative to the minimum of −68.68645 au at ϕ = 60°. [b] These very high energies, which arise from steric interactions between the carboxyl group and the C4 methyl, would be expected to make these conformations relatively inaccessible.



$$\overset{4}{\mathrm{C}}\mathrm{H_3}\overset{3}{\mathrm{C}}\mathrm{H_2}\underset{\mathrm{CH_3}}{\overset{\mathrm{OH}}{\mathrm{C}}}\text{—}\overset{*1}{\mathrm{C}}\mathrm{H_3}$$

1



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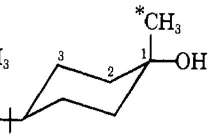

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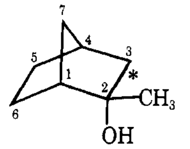

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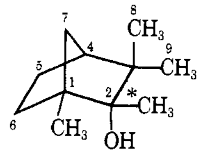

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minimum value of −52.74983 au (electronic plus nuclear repulsion) which occurs for ϕ = 75°. These semiempirical energies do not generally provide a quantitative representation of barriers hindering internal rotation, but their use in obtaining averaged coupling constants must be an improvement over the usual crude assumption that only the gauche and trans coupling constants be used in the average.

Calculated values of directly bonded, geminal, and vicinal $^{13}C-^{13}C$ coupling constants and energies in atomic units for butane and butanoic acid were obtained at 30° intervals of the dihedral angle ϕ, which is measured about the C2-C3 bonds. These results are entered in Tables II and III, respectively.

Results and Discussion

Experimental data for the series of alcohols **1–5** are tabulated in Table IV. Chemical shifts are measured in ppm from internal tetramethylsilane.

1. **Directly Bonded C–C Coupling Constants.** Experimental values of the directly bonded $^{13}C-^{13}C$ coupling constants in Table IV range from 38.5 to 41.4 Hz. Experimental values for ethane,[21] ethanol,[22] propane,[22] and 2-propanol[23] are 34.6, 37.3, 33 ± 2, and 38.4 Hz, respectively. Therefore, introduction of the OH functional group on one of the coupled carbon atoms produces a 3 to 5 Hz increase in the directly bonded coupling constants. The INDO–FPT results for 2-butanol in Table I are about 7 Hz greater than those for butane in Table II. This direction is consistent with the experimentally observed increase.

The usual correlation of directly bonded C–C coupling constants is with the product of the s characters of the bonding hybrid orbitals,[24] or, equivalently, to the square of the bond order between the valence shell s orbitals.[23] This type of description provides some interesting correlations, but it is based on some very crude approximations.[25,26] For example, it is based on the so-called "average energy approximation," which is used to eliminate the sum over the triplet states in the second order perturbation sum. Even if one uses this procedure it can be shown[26] that the neglect of orbital overlap compensates for the neglect of electron correlation.

More recent calculations of directly bonded C–C coupling constants[23,27,28] have also made use of the INDO–FPT method including noncontact contributions.[28] The orbital contributions are of importance in describing directly bonded C–C coupling in unsaturated and strained systems.[28]

Table IV. Carbon-13 Chemical Shifts[a] and $^{13}C-^{13}CH_3$ Coupling Constants[b] for Compounds 1–5

Compd		C1	C2	C3	C4	C5	C6	C7	C8	C9	C10
1	δ	29.8	71.0	37.6	9.7						
	J		38.5	2.4	1.9						
2[c]	δ	71.0	31.2	24.5	47.8						
	J	40.5	2.2	*d*	<0.4						
3[e]	δ	69.1	40.6	22.2	47.8						
	J	41.6	2.25	3.2	<0.4						
4[f]	δ	49.1	76.9	47.4	37.0	27.9	22.3	38.2			
	J	2.7	41.4	1.5	0.9	<0.35	1.8	<0.35			
5[g]	δ	52.0	79.8	42.9	49.2	25.5	29.4	41.0	26.6	26.3	16.0
	J	1.4	41.4	0.8	0.8	<0.4	0.9	0.4	5.4	<0.4	2.6

[a] In ppm to high frequency from TMS. [b] In hertz. [c] The ^{13}C-enriched methyl occurs at 24.7 ppm. The *tert*-butyl quaternary carbon and methyl carbon resonances occur at 31.7 and 27.2 ppm, respectively. [d] This splitting could not be resolved because of interference from other spectral lines. [e] Resonance for the ^{13}C-labeled methyl is at 31.0 ppm. The *tert*-butyl quaternary and methyl carbon resonances are at 32.0 and 27.2 ppm, respectively. [f] Resonance of the ^{13}C labeled methyl is at 30.4 ppm. [g] Resonance of the ^{13}C labeled methyl is at 22.1 ppm.

Variations by as much as 5-6 Hz are noted in the calculated results for directly bonded coupling constants as the dihedral angle is varied in Tables I-III. However, the fractional change is small, and it is not possible to say that these trends are present in the experimental results in Table IV.

2. Vicinal C-C Coupling Constants. The dependence of vicinal $^{13}C-^{13}C$ coupling constants on dihedral angle for compounds **1-5** was noted in a preliminary communication.[29] The magnitudes of the observed vicinal C-C coupling constants in Table IV range from a magnitude of 5.4 Hz to values too small to be measured (≤0.35-0.4 Hz). The experimental values from Table IV are entered in Table V along with estimated values of the dihedral angles and the calculated values for vicinal coupling in 2-butanol for the estimated dihedral angle. The latter were taken from Table I or were interpolated from Figure 1. However, in the case of 2-methyl-2-butanol (item 1 in Table I) a coupling constant of 2.03 Hz was obtained by Simpson's rule numerical integration from the formula

$$\langle J\rangle_{\mathrm{Av}} = \frac{\int_0^{2\pi} J(\phi)\exp[-V(\phi)/kT]\mathrm{d}\phi}{\int_0^{2\pi}\exp[-V(\phi)/kT]\mathrm{d}\phi} \qquad (2)$$

and the numerical data for $J(\phi)$ and $V(\phi)$ from Table I. This is in better agreement with the experimental value of 1.9 Hz than the previously estimated value of 2.4 Hz,[29] which was based on the overly simplified assumption that the 60, 180, and 300° rotamers would have equal populations.

The spread in values of vicinal coupling depending on dihedral angles indicates that these parameters have potential for structural studies provided that the other relevant factors can be identified. For example, the similarity of the calculated results for 2-butanol and butane in Tables II and III, respectively, suggests that substitution at the C2 and C3 carbon atoms will not be more important than for the analogous effect of substituents on vicinal H-H coupling. However, substitution at the C1 (or C4) carbon atom will have no analog in vicinal H-H coupling and may be expected to produce substantial effects because of the proximity of the orbitals on the C1 and C4 carbon atoms in conformations with dihedral angles near 0°. For example, the calculated value for the cis coupling in butanoic acid is only about one-third of the trans vicinal C-C coupling in Table III. For the assumed conformation of butanoic acid in which the carboxyl group is oriented so that the carbonyl eclipses the C3 carbon atom, the oxygen atom is in close proximity (1.70 Å) to the hydrogen atoms of the C4 carbon atom.[30] These steric effects lead to substantially higher energies for small values of the dihedral angles in Table III, and almost certainly provide additional, indirect mechanisms for the transmission of the coupling.

Table V. Comparison of Experimental Values of Vicinal C–C Coupling Constants for Compounds **1–5** with the Calculated Values for 2-Butanol for the Estimated Value of the Dihedral Angle ϕ

Compd	Carbon no. C_i	Dihedral angle ϕ, deg	$^3J(C_i-{}^*CH_3)$, Hz	
			Exptl	Calcd
1	4	*a*	1.9	2.0[a]
2	3	~ 180[b]	3.2	3.8
3	3	< 300[b]	*c*	1.5
4	4	120	0.9	1.4
	6	170	1.8	3.6
	7	275	<0.35	0.5
5	4	~ 125	0.8	1.4
	6	*d*	0.9	*d*
	7	~ 270	<0.4	0.5
	8	~0	5.4	5.3
	9	~90	<0.4	0.5
	10	~40	2.6	3.1

[a] The calculated value for 2-butanol (**1**) was obtained by numercal integration from eq 2 and the data in Table **I**. [b] Estimates for the dihedral angles were based on the assumption that the *tert*-butyl group produces sufficiently large steric interactions to give high statistical weights to the conformations **2** and **3**. [c] This splitting could not be resolved because of interference from other spectral lines. [d] This angle is difficult to estimate because of strong steric interactions between the labeled methyl and the C8 methyl in **5**.

Experimental values of vicinal $^{13}C-^{13}C$ coupling constants in a series of aliphatic and alicyclic carboxylic acids labeled in the carboxyl (C1) carbon[5] are consistent with the INDO-FPT results in Table III. For dihedral angles near 0° experimental values were 1.9 to 2.4 Hz to be compared with about 1.8 Hz in Table III, and for dihedral angles near 180° the experimental values ranged from 3.6 to 5.6 Hz.[5] The experimental data strongly suggested shifts of the maxima and minima away from the usual 180 and 90° values. This is probably due to a dependence on two dihedral angles associated with conformational readjustments in the carboxyl group. These effects would not be reflected in the calculated results in Table III.

In contrast to other types of vicinal coupling,[2-7] the simple form of eq 1 does not provide a completely adequate quantitative representation of the vicinal C-C coupling constants in the tables. As noted previously, it seems likely that there are other important factors affecting C-C coupling. There is now convincing experimental and theoretical evidence for the importance of direct[8] (electron-mediated) coupling which is dependent on both proximity and bond orientation effects.[31-35] Therefore, it is quite possible that for small values of the dihedral angles indirect[8] coupling, associated with the proximity and orientation of orbitals on atoms which are bonded to the coupled carbon atoms, is an important factor for vicinal C-C coupling, and leads to deviations from the form of eq 1. An analogous situation in the series of long range H-H coupling constants was encountered by Anet et al.[36] In a series of half-cage molecules with oxygen atoms both inside and outside, it was found that coupling was exceedingly small for protons separated by six to seven bonds. However, it was concluded[36] that interaction *through* an oxygen atom in one of the compounds led to appreciable coupling.

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Ab Initio SCF-MO Calculations on Carbanions. Methyl, Ethyl, Vinyl, and Ethynyl Anions[1]

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Abstract: The results of SCF-LCAO-MO calculations on methyl, ethyl, vinyl, and ethynyl anions are presented and compared with the parent hydrocarbons. The basis sets used include the minimum basis set, STO-4G, and extended basis sets of split shell (SS), including for some cases additional polarization functions, d on carbon (SS+d) and p on hydrogen (SS+d,p). Electron density and electron density difference functions are presented as three-dimensional perspective plots and are used to evaluate the electronic changes that occur on ionization of a C-H bond. Other energy quantities such as electron affinities and proton affinities are presented and discussed in addition to geometries and inversion barriers.

Carbanions are among the important intermediates in organic chemistry but their study presents a number of problems. The important class of conjugated carbanions is amenable to experimental study because such carbanions are relatively stable and are observable both as free anions and as ion pairs in solution and in the gas phase. They are also rather large molecular species from the quantum mechanical standpoint and ab initio calculations for a related series of such systems are presently feasible only with rather limited basis sets. Consequently, our study of such systems required a "calibration" study of simpler carbanions using a variety of basis sets. In this paper we present a study of methyl, ethyl, vinyl, and ethynyl anions using a consistent series of basis sets. No such study of a series of carbanions has yet been published although isolated members of this set have been studied on an individual basis. The most extensively studied of these is methyl anion.[2-7] Several important features have emerged from these studies; for example, with limited basis sets the highest occupied MO of CH_3^- is unbound. This result is known to be due to a truncated basis set[7] and a large basis that includes highly diffuse orbitals is required to bring this orbital down into binding range.[6] Nevertheless, even at the Hartree-Fock limit methyl anion has a higher energy than methyl radical; that is, the electron affinity of methyl radical is less than the correlation energy difference between radical and anion. In effect, in a