Experimental and Theoretical Studies of the Conformational and Substituent Dependencies of Vicinal ^{13}C–^{13}C Coupling Constants. Impinging Multiple Rear-Lobe Effects

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Abstract: Experimental and theoretical results are reported for a series of 1-substituted butyl compounds and for a series of 11-substituted 1-methyladamantane compounds. Experimental vicinal ^{13}C–^{13}C coupling constants were obtained from compounds having ^{13}C labels in the C1 and C11 (methyl) positions, respectively. Although the total variation of the coupling constants with substituents in each of the two series of compounds did not exceed 20%, vicinal coupling constants in the series of substituted butanes were uniformly *greater in magnitude* than those for the trans arrangement of the methyladamantanes. This was a surprising result which this study suggests has its origins in contributions of negative sign associated with the interactions of the rear lobes of the carbon hybrid orbitals. By means of the valence-bond bond-order formulation, which interrelates H–H and ^{13}C–^{13}C coupling constants, it is shown that a large number of direct (electron mediated) and indirect coupling paths contribute to vicinal ^{13}C–^{13}C coupling constants. The effects of conformations, substituents, and mechanism are also investigated in a number of compounds by means of the finite perturbation theory formulation in the INDO approximation of semiempirical molecular orbital theory. Calculated results for the trans arrangements of the carbons in the series butane, methylcyclohexane, and 1-methyladamantane are 4.27, 3.72, and 3.32 Hz, respectively. The monotonic decrease in the magnitudes of the coupling constants parallels the increase in the number of impinging carbon hybrid rear lobes in this series of compounds. The recognition of these effects also removes apparent anomalies in previous studies of vicinal ^{13}C–^{13}C coupling constants and further emphasizes the caution which must be used in relating vicinal ^{13}C–^{13}C coupling constants to dihedral angles.

In previous studies of vicinal ^{13}C–^{13}C coupling constants[2-4] the form of the conformational dependence was shown to be sensitive to the nature of the substituents and/or hybridization at the sites of the coupled carbon atoms. For example, in the series of aliphatic and alicyclic alcohols containing ^{13}C-labeled methyl groups it was found that the cis ^{13}C–^{13}C coupling constant is larger in magnitude than the trans value,[2b] whereas in the series of ^{13}C-carboxyl-labeled carboxylic acids[2a] the cis coupling constant is only about one-half of the trans value. Clearly, the physical situation presented by coupling between vicinal carbons is much more complicated than coupling between vicinal protons so that further experimental and theoretical work is required before coupling between vicinal carbons can be used with reliability for studies of molecular conformations in solution.

The present study extends the previous work[2-4] by including experimental and theoretical studies of vicinal ^{13}C–^{13}C coupling constants in a series of ^{13}C-labeled 1-substituted butanes and ^{13}C-labeled 11-substituted 1-methyladamantanes. In compounds with the same substituents the ^{13}C–^{13}C coupling constants in the butyl series were 1.2–1.4 Hz greater than those in the 1-methyladamantane series. This was quite surprising since the latter conforms to the trans arrangement of the vicinal carbons, which should be the upper limit for the butyl values. This apparently anomalous behavior was investigated theoretically by both valence-bond (VB) and molecular-orbital (MO) techniques.

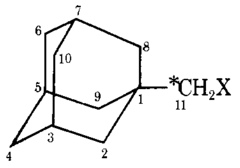
The VB bond-order formulation[5] for Fermi contact coupling is not only useful for interpreting coupling-constant mechanisms, it also allows one to relate ^{13}C–^{13}C coupling constants to H–H coupling constants for which there is a more extensive experimental and theoretical literature. Molecular-orbital results in the finite perturbation theory (FPT) formulation for coupling constants in the parent and representative substituted and cyclic compounds provide a numerical assessment of the relevant factors and show that the apparent disparities between the conformational dependencies in the aliphatic and multicyclic series are due to the interactions between the rear lobes of the several carbon hybrid orbitals in the later series.

I. Experimental Vicinal ^{13}C–^{13}C Coupling Constants

A. C1-Labeled, C1-Substituted Butanes. Experimental values of vicinal ^{13}C–^{13}C coupling constants between the C1 and the C4 carbon atoms in the series of substituted butanes **1–6** are entered in Table I.[6] The formula numbers are given in parentheses in the table. The syntheses and spectral analyses of these compounds are discussed in the Experimental Section. From the results in Table I it is to be noted that the values of $^3J_{CC'}$ cover the fairly narrow range of 4.3–5.2 Hz for a rather diverse set of substituents. These extremes occur for X = F and Br, respectively, so that the range in values may not reflect any sort of genuine electronic substituent effects rather than the effects of substituent size on the populations of the rotamers. However in Section II it will be shown from MO results that small electronic perturbations would be expected, especially for certain orientations of 1-fluorobutane (**3**).

$CH_3CH_2CH_2{}^*CH_2X$

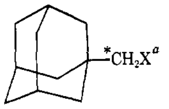
1–6



7–11

B. C11-Labeled, C11-Substituted 1-Methyladamantanes. Experimental values for the vicinal ^{13}C–^{13}C coupling constants for ^{13}C-labeled 1-methyladamantanes **7–11** are also entered in Table I. In this series the range of coupling-constant values with substituents is only 3.2–3.7 Hz, which provides even further indication that the direct electronic perturbation of the electronic environment is a less important factor than the size of the substituent on the rotamer populations. As noted above,

Table I. Experimental Values of Vicinal $^{13}C-^{13}C$ Coupling Constants in a Series of ^{13}C C1-Labeled, C1-Substituted Butanes **1**–**6** and a Series of ^{13}C C11-Labeled, C11-Substituted 1-Methyladamantanes **7**–**11**

X	$CH_3CH_2CH_2{}^*CH_2X^a$ $^3J_{CC'}$, Hz	 $^3J_{CC'}$, Hz
H		3.2^b $(\mathbf{7})^e$
OH	4.6^c $(\mathbf{1})^d$	3.3 $(\mathbf{8})^e$
CN	4.7 $(\mathbf{2})^d$	3.4 $(\mathbf{9})^g$
F	4.3 $(\mathbf{3})^f$	
Cl	4.8^c $(\mathbf{4})^d$	3.4 $(\mathbf{10})^g$
Br	5.2^c $(\mathbf{5})^d$	
I	4.9^c $(\mathbf{6})^d$	3.7 $(\mathbf{11})^g$

[a] Structural formula numbers are given in parentheses after the coupling-constant values. [b] D. M. Doddrell, E. W. Della, and M. Barfield, unpublished results, 1975. [c] Reference 3. [d] Chemical shifts previously reported in ref 30. [e] Chemical shifts previously reported in ref 31 b. [f] Chemical shifts for C1, C2, C3, and C4, respectively: 83.4, 33.4, 19.3, and 13.8. [g] Chemical shifts for C1, C2, C3, C4, and C11, respectively, for **9**: not seen, 42.2, 29.2, 37.0, and 32.0; for **10**: 33.5, 39.6, 28.6, 37.4, and 73.7; for **11**: not seen, 42.4, 29.4, 37.2, and 26.8.

the most surprising feature of the experimental results in Table I is that the values for the 1-methyladamantanes are 1.2–1.4 Hz *less* than the vicinal coupling constants for the corresponding substituted butanes. This is just the opposite of that which would have been predicted on the basis of our previous investigations.[2-4] The butyl values must reflect average values, in which the form of the conformational dependence is weighted with respect to the barrier which hinders internal rotation. In almost all cases the gauche and trans conformations are of lower energy and make the most important contributions to the average. In all of the experimental and theoretical studies[2-4] it has been found that the gauche $^{13}C-^{13}C$ coupling constants are smaller in magnitude than the trans values. As a consequence, the vicinal $^{13}C-^{13}C$ coupling constants in the butyl compounds should actually be less than those in the 1-methyladamantanes in contrast to that which is noted for the data in Table I. In the subsequent sections it will be shown that this disparity is due to the unique electronic features associated with the trans arrangements in cyclic compounds such as methylcyclohexane and 1-methyladamantane.

II. Theoretical Results for Vicinal $^{13}C-^{13}C$ Coupling Constants

A. A Valence-Bond Bond-Order Formulation. The Relationship of $^{13}C-^{13}C$ Coupling Constants to H–H Coupling Constants. The VB bond-order formulation,[5] which makes use of the relationship of Fermi contact coupling to Penney–Dirac bond orders,[7] has been used to provide a conceptual basis for discussing mechanisms of nuclear spin-spin coupling, i.e., *indirect* and *direct* (electron-mediated) mechanisms. Furthermore, this method can be used to interrelate different types of coupling constants,[8,9] which precludes the necessity for the explicit calculations of molecular wave functions. For example, this has been shown to be a most convenient procedure for investigation of the very complicated situation found for $^{13}C-^{19}F$ coupling in aromatic systems[9] and the development here will parallel that one.

For molecular systems in which there are only small deviations from a localized bond description, coupling constants are related to nonlocal Penney–Dirac bond orders for four-electron fragments.[9] The theoretical results of ref 5 can be generalized immediately to the cases in which there is more than one atomic orbital on each of the coupled nuclei, such that up to second order in the bond orders,

$$J_{CC'} = K(\Delta E)^{-1}\left[\sum_{i,k} p^0(c_i,c_k) + (3/2)\sum_{i,j,k} p^0(c_i,\sigma_j)p^0(\sigma_j{}',c_k)\right] \quad (1)$$

where K is a constant which depends on the magnetogyric ratios of the coupled carbons, the s-orbital densities at the two nuclei, and physical constants which do not depend on the nuclei or the electronic features of the molecule. The term ΔE in eq 1 is called the "average excitation energy". Because this quantity cannot be calculated, justification for this formulation depends on its cancellation in the final coupling-constant expression.[5,10] The fragment bond orders $p^0(c_i,c_k)$ under the first summation in eq 1 arise for the four-electron fragments $[h_i\text{-}c_i, c_k\text{-}h_k]$, for example, associated with bonds i and k on the coupled carbon atoms. Contributions from these terms have been called *direct* (electron mediated)[5] and since there are four bonds on each tetrahedral carbon, there will be 16 such terms. These direct terms are expected to dominate $^3J_{CC'}$.

The second summation in eq 1 includes a sum over all the other bonds $\sigma_j\text{-}\sigma_j{}'$ with orbitals σ_j and $\sigma_j{}'$. As these terms each involve an intermediary bond in the transmission of the coupling, they have been termed indirect.[5] In the case of the butane molecule with five bonds other than those associated with a pair of carbon atoms, there would be 100 such terms in the summation in eq 1.

To relate the $^{13}C-^{13}C$ coupling constants to H–H coupling constants, it is necessary to consider the analogous relationship of the latter to the bond orders,

$$J_{HH'} = K'(\Delta E)^{-1}\left[p^0(h,h') + (3/2)\sum_j p^0(h,\sigma_j)p^0(\sigma_j{}',h')\right] \quad (2)$$

where $p^0(h,h')$ is the fragment bond order associated with the fragment $[h\text{-}c, c'\text{-}h']$ and the other terms have definitions analogous to those given in eq 1. From eq 20 of ref 5 the fragment bond orders in eq 1 are related to those in eq 2 by the expressions,

$$p^0(c_i,c_k) = (-1)^{n_i+n_k}p^0(h_i,h_k) \quad (3)$$

$$p^0(c_i,\sigma_j) = (-1)^{n_i}p^0(h_i,\sigma_j) \quad (4)$$

$$p^0(\sigma_j{}',c_k) = (-1)^{n_k}p^0(\sigma_j{}',h_k) \quad (5)$$

where n_i is equal to zero if the hydrogenic orbital h_i replaces c_i and equal to one if the orbital c_i is directed toward orbital h_i. Obviously, n_k is defined in the same way for bond k.

On substituting eq 3–5 into eq 1 and moving the summation over bonds i and k outside of the brackets, the $^{13}C-^{13}C$ coupling constants are related to the fragment bond orders associated with the hydrogenic orbitals by the expression

$$J_{CC'} = K(\Delta E)^{-1}\sum_{i,k}(-1)^{n_i+n_k}\left[p^0(h_i,h_k) + (3/2)\sum_j p^0(h_i,\sigma_j)p^0(\sigma_j{}',h_k)\right] \quad (6)$$

The expression in brackets in eq 6 also occurs in eq 2, so that we may write an expression for the $^{13}C-^{13}C$ coupling constants

$$J_{CC'} = (K/K')\sum_{i,k}(-1)^{n_i+n_k}J(H_i,H_k) \quad (7)$$

where the summation runs over all of the pairs of coupling constants $J(H_i,H_k)$ between the hydrogen atoms directed toward the carbon atoms C and C′ and also the coupling constants which would occur if protons replaced the coupled car-

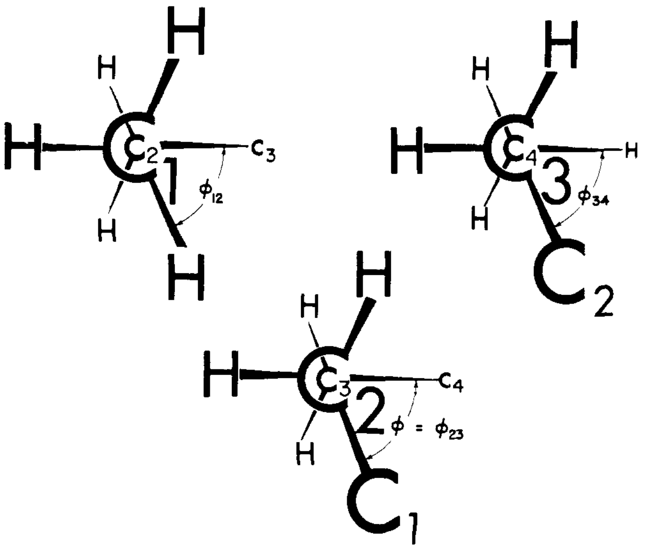


Figure 1. Designation of the dihedral angles $\phi = \phi_{12}$, ϕ_{23}, and ϕ_{34} about the various C-C bonds in butyl fragments.

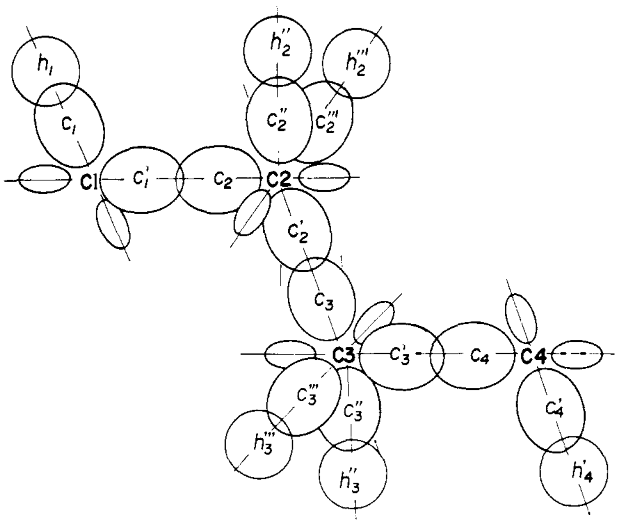


Figure 2. Designation of orbitals in an 18-orbital moiety of butane. The trans arrangement is depicted to show the favorable orientation of "rear lobes" of c_1–c_3' and c_2–c_4'.

bon atoms. This type of nonisotopic replacement would correspond to changes in the intervening electronic structure. This is a weak assumption, which has been used in previous descriptions[11,12] as the *only* term relating carbon coupling constants to those involving hydrogen. Equation 7 is more general than the previous ones and it should also be noted that the cancellation of the "average excitation energies" in this expression implies that these would be the same for both types of coupling. This assumption would affect the calculated magnitudes, but not the discussion of coupling paths, which is the major theme of this section. Even though there are some ill-defined approximations implicit in the development of eq 7, it is of general applicability and avoids the sometimes well-defined but often crude approximations of certain molecular quantum-mechanical descriptions.

Of the 16 terms which occur in the expression for ^{13}C–^{13}C vicinal coupling between two tetrahedral carbon atoms, one corresponds to vicinal H–H coupling ($^3J_{HH'}(\phi)$), six to long-range H–H coupling over four bonds, and nine terms to long range coupling over five bonds. Therefore, the expression for $^3J_{CC'}(\phi)$ for the all-trans arrangement of butane is related to the various $J_{HH'}$ by

$$\begin{aligned} {}^3J_{CC'}(\phi) = (K/K')[&{}^3J_{HH'}(\phi) - {}^4J_{HH'}(60°,\phi) - {}^4J_{HH'}(180°,\phi) \\ &- {}^4J_{HH'}(300°,\phi) - {}^4J_{HH'}(\phi,60°) - {}^4J_{HH'}(\phi,180°) \\ &- {}^4J_{HH'}(\phi,300°) + {}^5J_{HH'}(60°,\phi,60°) + {}^5J_{HH'}(60°,\phi,180°) \\ &+ {}^5J_{HH'}(60°,\phi,300°) + {}^5J_{HH'}(180°,\phi,60°) \\ &+ {}^5J_{HH'}(180°,\phi,180°) + {}^5J_{HH'}(180°,\phi,300°) \\ &+ {}^5J_{HH'}(300°,\phi,60°) + {}^5J_{HH'}(300°,\phi,180°) \\ &+ {}^5J_{HH'}(300°,\phi,300°)] \qquad (8) \end{aligned}$$

In eq 8 the dihedral angle measured about the C2–C3 bond is denoted by ϕ and the other angles given in parentheses denote dihedral angles measured about the C1–C2 and C3–C4 bonds, respectively. The dihedral angles about the various C–C bonds are depicted in Figure 1. It will be useful to consider in turn the relative importance and conformational dependencies for coupling over three, four, and five bonds in eq 8.

The conformational dependence of vicinal H–H coupling has been used extensively for studies of molecular conformation in solution. This is possible because of the relatively simple and reproducible trigonometric dependence on dihedral angle[13,14]

$$^3J_{HH'}(\phi) = A\cos^2\phi + B\cos\phi + C \qquad (9)$$

where A, B, and C depend on substituents, hybridization, etc., but the magnitudes of B and C are much less than A. Since B is negative, the trans coupling is somewhat larger than the cis coupling constant. Although the many other terms in eq 8 will modify the form of the angular dependence of $^3J_{CC'}$, the largest contributions are expected to be due to this first term.

The next six terms in eq 8 involve long-range H–H coupling over four bonds. The physical situation presented by this type of coupling is much more complicated than vicinal coupling. Theoretical studies of $^4J_{HH'}$, which were based on both VB[15] and INDO-FPT[16] MO descriptions were found not to be consistent with detailed experimental results.[17] A new formulation was presented[17] which analyzed the various mechanisms involved, including the conformational dependencies of those mechanisms. Because the terms associated with $^4J_{HH'}$ in eq 8 are important for negative contributions to $^3J_{CC'}$, it will be important to consider them in more detail here.

The substantial (~2 Hz) $^4J_{HH'}$ coupling constants are of positive sign and occur for the "W" arrangements of the carbons in a propanic fragment. At an early stage these were presumed to be associated with direct interactions of the "rear lobes" of the carbon hybrid orbitals on C1 and C3, which are directed toward the coupled protons.[18] The difficulties in theoretical studies of this type of coupling have been shown to be due to the cancellations between large terms of opposite sign for this conformation. For most other conformations $^4J_{HH'}$ are small and negative.[17]

The implications of these contributions for vicinal ^{13}C–^{13}C coupling constants follow from eq 8 and Figure 2. Figure 2 includes the designations of the orbitals in an 18-orbital moiety of the butane molecule in an all-trans conformation. The direct interaction of the rear lobe of c_1 (which is centered on carbon C1) with c_3' (which is directed toward carbon C4) and of c_2 (which is directed toward carbon C1) with c_4' (which is centered on C4) make negative contributions to the vicinal ^{13}C–^{13}C coupling constant between carbons C1 and C4 in the all-trans arrangement. This follows from the third and sixth terms in brackets in eq 8, since $^4J_{HH'}(180°,180°)$ is positive in sign. The other values of $^4J_{HH'}$ are small and negative and will give even smaller, positive contributions to $^3J_{CC'}(180°)$ according to eq 8. The overall effect of the four-bond H–H coupling-constant terms on $^3J_{CC'}(180°)$ is to decrease the value below that from the three-bond contribution, but this will quickly disappear on rotation about any one of the three bonds as the condition for overlap of the "rear lobes" is less favored.

Because of the small amount of experimental data for long-range H-H coupling over five bonds in saturated hydrocarbons and because these parameters depend on three dihedral angles, there have been few attempts at systematic theoretical investigation. The valence-bond bond-order description[5] gave a maximum value of 1 Hz for ${}^5J_{HH'}(180°,\phi,180°)$, independent of the value of ϕ, and the other terms were expected to give even smaller contributions. However, as the dihedral angle ϕ becomes small, the protons on the C1 and C4 carbon atoms become spatially proximate. As a consequence, the five-bond terms provide important contributions to ${}^3J_{CC'}$ for values of the dihedral angle close to 0°. Numerical estimates of these various effects will be based on MO results given in the next section.

If atomic orbital densities are based on SCF values,[19] the ratio of the coefficients in eq 7 and 8 is given by

$$K/K' = [\gamma_C{}^2\phi_{2s}{}^2(\mathrm{C})/\gamma_H{}^2\phi_{1s}{}^2(\mathrm{H})] = 0.178 \qquad (10)$$

where γ_C and γ_H are the magnetogyric ratios and $\phi_{2s}{}^2(\mathrm{C})$ and $\phi_{1s}{}^2(\mathrm{H})$ are the theoretical values of the densities. For reasonable values of the vicinal and long-range H-H coupling constants in eq 8 [${}^3J_{HH'}(180°) = 12$ Hz, ${}^4J_{HH'}(180°,180°) = 2$ Hz, ${}^4J_{HH'}(60°,180°) = {}^4J_{HH'}(180°,60°) = {}^4J_{HH'}(300°,180°) = {}^4J_{HH'}(180°,300°) = -0.5$ Hz, ${}^5J_{HH'}(180°,\phi,180°) = 1$ Hz, and assuming that the eight other values of ${}^5J_{HH'}$ are negligible], the theoretical factor of 0.178 in eq 8 gives a value of ${}^3J_{CC'}(180°) = 2$ Hz, which is low by almost a factor of two. However, it is possible that this could simply be a consequence of the unjustified neglect of the many five-bond terms in eq 8. Taking a rotational average of the H-H coupling constants, then the appropriate values are the 8 Hz value for ethane,[20] a value $\leq \pm 0.2$ Hz for ${}^4J_{HH'}$ in propane,[21] and a negligible value of ${}^5J_{HH'}$ in butane, then the average value of ${}^3J_{CC'}$ from eq 8 is 1.4 Hz, which is smaller (as expected) than the calculated trans ($\phi = 180°$) value, but it is only about one-third of the experimental values in Table I. Better numerical agreement is noted from the MO calculations to be discussed in the subsequent sections.

B. Molecular-Orbital Results for Vicinal ${}^{13}C-{}^{13}C$ Coupling Constants in Model Compounds. Molecular-orbital calculations of vicinal ${}^{13}C-{}^{13}C$ coupling constants for a number of model compounds were based on the finite perturbation formulation (FPT)[22] in the INDO (intermediate neglect of differential overlap) approximation of self-consistent-field (SCF) molecular orbital (MO) theory. Bond distances and bond angles were based on the standard geometrical model[23] unless specified otherwise.

1. Conformational Dependencies of the Coupling Constant Contributions in Butane. The calculated INDO-FPT results for vicinal ${}^{13}C-{}^{13}C$ coupling ${}^3J(\mathrm{C1-C4})$ between the C1 and C4 carbon atoms of butane, taken to be representative of compounds **1-6** in Table I, are entered in the second column (i) of Table II at 30° intervals of the dihedral angle ϕ.[24] The dihedral angle ϕ is measured about the C2-C3 bond as depicted in Figure 1. Calculated values of the directly bonded and geminal ${}^{13}C-{}^{13}C$ coupling constants, as well as the INDO energies, are also given in ref 3. It was noted previously[2b] that the trend to larger cis than trans ${}^{13}C-{}^{13}C$ coupling constants in butane is completely consistent with that predicted and observed in the series of alicyclic and aliphatic 2-butanols.

It has been noted previously[17,25,26] that it is possible to make at least qualitative arguments about the relative importance of the many possible coupling paths in a procedure which sets various overlap integrals to zero. This has the effect of making identically zero those associated resonance integrals which enter the Fock matrices because of the assumption of their proportionality to overlap integrals in semiempirical schemes, which invoke the approximation of the neglect of differential overlap. Clearly, this cannot be done for bonded atoms, as the energy would increase, the bonding in the molecule would be disrupted, and the calculated coupling constants would be meaningless. In all of the calculations described here the energy variations were less than 0.05 au.

Table II. Vicinal ${}^{13}C-{}^{13}C$ Coupling Constants in Butane Calculated as a Function of the Dihedral Angle ϕ and Including Several Modifications in the INDO–FPT Scheme

Dihedral angle ϕ, deg	i,[a] Hz	ii,[b] Hz	iii,[c] Hz	iv,[d] Hz	v,[e] Hz
0	5.79	7.79	8.60	2.22	3.73
30	3.96	5.33	6.09	1.81	2.75
60	1.97	2.01	2.54	1.00	0.86
90	0.56	0.43	0.59	0.62	0.31
120	1.45	2.28	2.28	2.47	2.32
150	3.34	5.40	5.40	5.52	5.45
180	4.27	6.84	6.85	6.94	6.89

[a] These results are taken from the unmodified INDO–FPT program. [b] All overlap integrals between valence atomic orbitals on the C1 and C3 carbon atoms and the C2 and C4 carbon atoms were set equal to zero. [c] In addition to the procedure of footnote *b*, all overlap integrals between valence atomic orbitals on the C1 and C4 carbon atoms were set equal to zero. [d] In addition to the procedure of footnote *c*, all overlap integrals between the hydrogen atoms centered on the C1 carbon atom and those centered on the C4 carbon atom were set equal to zero. [e] In addition to the procedure of footnote *d*, overlap integrals were set equal to zero between the valence atomic orbitals of the C1 carbon and the hydrogenic orbitals bonded to the C4 carbon, and the valence atomic orbitals of the C4 carbon and the hydrogenic orbitals bonded to the C1 carbon.

(ii) In the second set of calculations for the butane molecule, all overlap integrals (these are proportional to resonance integrals in the Fock matrices[26]) between valence atomic orbitals on the C1 and C3 carbon atoms and the C2 and C4 carbon atoms were set equal to zero and the calculated results at 30° intervals of the dihedral angle were entered in Table II. For dihedral angles of 0 and 180° the vicinal ${}^{13}C-{}^{13}C$ coupling constants increase by 2.0 and 2.5 Hz, respectively. In fact, it may also be noted from Table II that the increase in the trans coupling constant is not significantly changed by the subsequent modifications of the integrals. Therefore, it must be concluded that the direct (electron-mediated) mechanisms associated with the interactions of the "rear lobes" of the C1-C3 and C2-C4 orbitals in the hybrid orbital picture of Figure 2 make negative contributions to the ${}^{13}C-{}^{13}C$ coupling constants. This is in complete conformity with the conclusions of the VB method, but the effect is approximately −2.5 Hz, which is a larger magnitude than might have been inferred from the VB description. Clearly, these semiempirical MO schemes use a basis set of valence shell *atomic orbitals* on each of the carbon atoms rather than the hybrid orbitals depicted in Figure 2, but this should not affect the conclusions regarding mechanisms.

(iii) In the third set of INDO-FPT calculations with results in the fourth column of Table II, all overlap integrals between valence atomic orbitals on the C1 and C4 carbon atoms of butane were *also* set equal to zero and the calculations repeated as a function of the dihedral angle. From Table I it can be seen that the trans ${}^3J_{CC'}$ coupling constant is changed only slightly, whereas the value for $\phi = 0°$ is increased by another 0.8 Hz due to direct interactions between the atomic orbitals on C1 and C4 in the proximate orientations.

(iv) In the fourth set of INDO-FPT calculations for butane it was recognized that the hydrogen atoms bonded to the C1 and C4 carbon atoms are in close proximity for the cis arrangement and could provide a possible route for direct (electron-mediated) coupling between the two vicinal carbons. Accordingly, all overlap integrals between the three hydrogens on C1 and the three hydrogens on C4 were set equal to zero and the calculations repeated as a function of the dihedral angle.

These results in Table II show a decrease of ${}^3J_{CC'}(0°)$ by more than 6 Hz, which is in complete accord with our previous suggestion[2,3] that this would prove to be an important direct mechanism for vicinal ${}^{13}C-{}^{13}C$ coupling. It also explains why the cis coupling in butane is larger than the trans value.

(v) In the final set of INDO-FPT calculations in butane all overlap integrals between the hydrogenic 1s atomic orbitals on C1 and the valence atomic orbitals on C4, as well as the overlap integrals between the hydrogenic 1s atomic orbitals bonded to C4 and the valence atomic orbitals of C1, were set equal to zero. These results are entered in the last column of Table II. There is a slight increase in the values of the vicinal coupling constants for small values of the dihedral angle and a negligible effect for angles near the trans arrangement. The results in this column should provide a crude measure of the remaining type of direct mechanism important for vicinal coupling in addition to the smaller indirect mechanisms. The calculated results in the last column of Table II can be reproduced to within 0.09 Hz by the expression

$$ {}^3J_{CC'}{}^{(v)}(\phi) = 5.00 \cos^2\phi - 1.58 \cos\phi + 0.31 \qquad (11)$$

which is of the same general trigonometric form as that for vicinal H-H coupling constants.[13,14] This simple form only arises for vicinal ${}^{13}C-{}^{13}C$ coupling on removing the many important non-next-nearest-neighbor interactions.

Because of the importance of the "rear-lobe" interactions for vicinal ${}^{13}C-{}^{13}C$ coupling constants, twisting of the methyl groups away from the all-trans arrangement depicted in Figure 2 would have the effect of decreasing the importance of these interactions and giving an increase in the vicinal ${}^{13}C-{}^{13}C$ coupling constants for $\phi = 180°$. To investigate the quantitative implications of this prediction, INDO-FPT results for ${}^3J(C1-C4)$ in butane were obtained for a number of conformations in which one or both of the methyl groups were twisted away from the all-trans arrangement ($\phi_{12} = \phi_{23} = \phi_{34} = 180°$, where these dihedral angles are measured about the C1-C2, C2-C3, and C3-C4 bonds, respectively, as depicted in Figure 1). Calculated results, which were obtained for the trans ($\phi = \phi_{23} = 180°$) and the *gauche* ($\phi = \phi_{23} = 60°$) arrangements for a number of values of the dihedral angles ϕ_{12} and ϕ_{34}, are entered in Table III along with values of the total calculated energies $V(\phi_{12},\phi_{23},\phi_{34})$ in atomic units. The coupling constants increase, as expected, with the greatest increase of about 0.7 Hz occurring for the relatively high-energy situation for which $\phi_{12} = \phi_{34} = 120°$. The effects of rotational averaging on ${}^3J_{CC'}(\phi)$ were investigated by means of the equation

$$\langle {}^3J(\phi_{23})\rangle = \frac{\int_0^{2\pi}\int_0^{2\pi} {}^3J(\phi_{12},\phi_{23},\phi_{34}) \exp[-V(\phi_{12},\phi_{23},\phi_{34})/kT]\, d\phi_{12} d\phi_{34}}{\int_0^{2\pi}\int_0^{2\pi} \exp[-V(\phi_{12},\phi_{23},\phi_{34})/kT]\, d\phi_{12} d\phi_{34}} \qquad (12)$$

where values for ${}^3J(\phi_{12},\phi_{23},\phi_{34})$ and $V(\phi_{12},\phi_{23},\phi_{34})$ are given in Table III.[27] For the case in which $\phi_{23} = 180°$ the data from Table III in eq 12 lead to calculated vicinal coupling constants of $\langle {}^3J_{CC'}(180°)\rangle = 4.32$ and 4.36 Hz, corresponding to averaging over the motion of one or two methyl groups, respectively.[28] Thus, it can only be concluded that there is a slight effect on the rotationally averaged coupling arising from the "rear-lobe" interactions of the methyl groups, but that the difference is not sufficient to warrant the much greater expense of this refinement. This conclusion is used in the subsequent discussion of ${}^{13}C-{}^{13}C$ coupling in substituted butanes.

2. Dependence of Vicinal ${}^{13}C-{}^{13}C$ Coupling Constants on Substituent Orientation in 1-Fluorobutane and Valeronitrile. Calculated INDO-FPT results for vicinal ${}^{13}C-{}^{13}C$ coupling constants in 1-fluorobutane (**3**) and valeronitrile (**2**) are entered in Table IV for 30° intervals of the dihedral angle $\phi = \phi_{23}$, and with $\phi_{12} = 60$, 180, and 300°. Since the 1-fluorobutane results exhibit some striking differences from the butane results, these are also plotted in Figure 3 as a function of the dihedral angle ϕ. Of particular interest is the very substantial fluorine positional dependence, which has its maximum positive effect for the case in which C1 and C4 are cis and $\phi_{12} = 180°$, and its maximum negative effect when the substituent is gauche. Clearly, these effects must be of the same general type as those found for ${}^3J_{CC'}(0°)$ for butane in the previous section, but the magnitudes of the effects seem to be amplified by the presence of the fluorine substituent. Unfortunately, there is not yet experimental data to compare with these results.

The results for ${}^3J_{CC'}(\phi)$ in valeronitrile in Table IV, in contrast to those for 1-fluorobutane, are more nearly like those for butane in Table II. For the cis arrangement of C1 and C4,

Table III. INDO-FPT Results for Vicinal ${}^{13}C-{}^{13}C$ Coupling Constants in Butane for Several Orientations of the Two Methyl Groups

Dihedral angles,[a] deg			${}^3J$(C1-C4), Hz	Energy, V,[b] au × 10^3
ϕ	ϕ_{12}	ϕ_{34}		
180	180	180	4.27	0.000
180	180	175	4.27	0.066
180	180	170	4.29	0.260
180	180	165	4.32	0.568
180	180	160	4.36	0.969
180	180	150	4.45	1.939
180	180	120	4.64	3.881
180	150	150	4.63	3.874
180	150	120	4.83	5.823
180	120	120	5.02	7.766
60	180	180	1.94	0.171
60	180	165	2.37	1.807
60	180	150	2.64	3.614
60	180	120	2.13	3.777
60	180	90	1.57	0.677

[a] Dihedral angles are defined in Figure 1. [b] Energy values are relative to the minimum of −35.16839 au for $\phi = \phi_{12} = \phi_{34} = 180°$.

Table IV. Vicinal ${}^{13}C-{}^{13}C$ Coupling Constants in 1-Fluorobutane and Valeronitrile Calculated as a Function of the Dihedral Angles ϕ_{23} and ϕ_{12} in the INDO-FPT Scheme.

Dihedral angles,[a] deg		1-Fluorobutane ${}^3J$(C1-C4), Hz	Valeronitrile[b] ${}^3J$(C1-C4), Hz
ϕ_{23}	ϕ_{12}		
0	60	3.66	6.49
	180	7.40	5.96
	300	3.66	6.49
30	60	3.31	4.45
	180	5.16	4.08
	300	2.21	4.53
60	60	1.96	2.00
	180	2.37	1.99
	300	0.82	2.21
90	60	0.58	0.54
	180	0.56	0.55
	300	0.51	0.56
120	60	1.39	1.40
	180	1.79	1.48
	300	1.60	1.53
150	60	3.33	3.32
	180	4.22	3.46
	300	3.46	3.45
180	60	4.33	4.31
	180	5.39	4.42
	300	4.33	4.31

[a] These are defined as in Figure 1. [b] The single and triple bond distances in $-CC{\equiv}N$ were taken to be 1.464 and 1.157 Å, respectively.

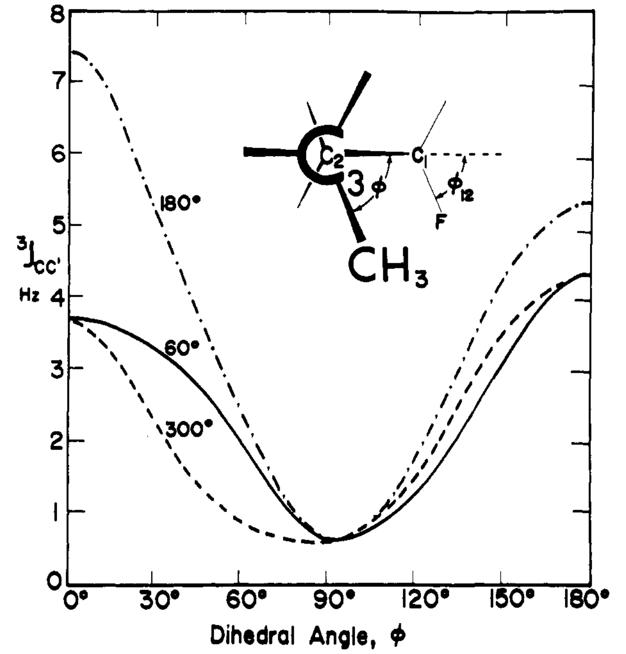


Figure 3. A plot of calculated vicinal ^{13}C-^{13}C coupling constants in 1-fluorobutane vs. dihedral angle ϕ = (ϕ_{23}) for three orientations of the fluorine, ϕ_{12} = 60, 180, and 300°. The dihedral angles are depicted in the inset diagram.

for example, the maximum change in $^3J_{CC'}(0°)$ with orientation of the CN function is only about 0.5 Hz. It is predicted that CN substitution at the 1-position will not have very much effect on vicinal ^{13}C-^{13}C coupling constants. This is consistent with the results in the methyladamantane series in Table I.

To compare the calculated results from Table IV with the experimental values in Table I, it is necessary to perform an average over the dihedral angles ϕ_{12} and ϕ_{23}. As was discussed in the previous section, an average over ϕ_{34} would be expected to increase the value of $\langle ^3J_{CC'}\rangle$ only negligibly. Simpson's rule numerical integration with a 30° grid for ϕ_{23} and for ϕ_{12} = 60, 180, and 300° in the equation

$$\langle {}^3J_{CC'}\rangle = \frac{\int_0^{2\pi}\int_0^{2\pi} {}^3J(\phi_{12},\phi_{23})\exp[-V(\phi_{12},\phi_{23})/kT]d\phi_{12}d\phi_{23}}{\int_0^{2\pi}\int_0^{2\pi}\exp[-V(\phi_{12},\phi_{34})/kT]d\phi_{12}d\phi_{34}} \qquad (13)$$

yields values of 3.80 and 2.35 Hz for 1-fluorobutane and valeronitrile, respectively. The experimental values in Table I, in comparison, are 4.3 and 4.7 Hz, respectively. The latter value is just twice the calculated one, and this is, perhaps, the most disparate value noted in the comparisons of calculated and experimental values of ^{13}C-^{13}C coupling constants in the aliphatic series. This inadequacy may be due to the incorrect prediction of a higher energy for the trans than for the gauche arrangement of this molecule in the INDO computational scheme.

3. The Effects of Impinging Multiple Rear Lobes on $^3J_{CC'}$ in Methylcyclohexane and Methyladamantane. It was noted previously that the impinging of the rear lobes of the carbon hybrid orbitals in the trans arrangement of butane produces contributions of negative sign to the vicinal ^{13}C-^{13}C coupling constant. The situation in methylcyclohexane and 1-methyladamantane is depicted in Figures 4a and 4b. In these cases, however, three and four lobes, respectively, impinge in the center of the rings. Evidence exists[29] that the back lobes interact in adamantyl carbonium ions and carbanions, and hence one might anticipate a particularly significant impinging effect in the present study. From the VB bond-order formulation of Section IIA one would expect a negative sign for contributions of this type. This can be seen by inspecting the terms in the second summation of eq 1 and noting that $p^0(\sigma_j',c_k) = -p^0(\sigma_j,c_k)$, where σ_j denotes the carbon hybrid orbitals (σ_j' would correspond to hydrogens for the cases depicted in Figure 4) having back lobes directed toward the back lobes of the hybrid orbitals c_i and c_k, which are associated with the bonds containing the coupled nuclei C and C′. Because of the symmetry of these molecules and the way that they enter the summation in eq 1, they would also be expected to be approximately additive with the number of impinging rear lobes. This argument is almost identical with the one which was used to describe the negative and approximately additive contributions of adjacent π bonds on geminal H-H coupling constants in substituted methanes.[14]

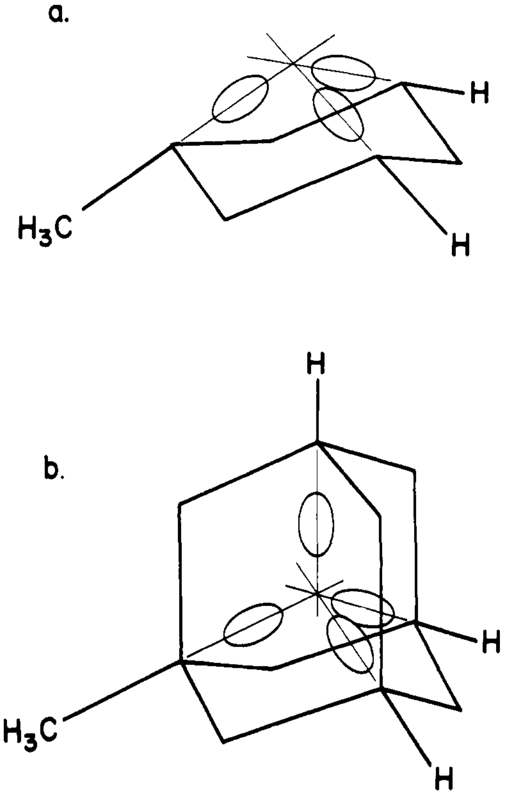


Figure 4. Schematic representation of the impinging rear lobes in (a) methylcyclohexane and (b) 1-methyladamantane.

To investigate the importance of multiple rear lobes on the vicinal ^{13}C-^{13}C coupling constants, INDO-FPT calculations were performed for the coupling between the methyl-group carbon and the carbon separated by three bonds in methylcyclohexane and methyladamantane. These results are entered in Table V along with the calculated value for $^3J_{CC'}(180°)$ from Table II.

The calculated value of the vicinal ^{13}C-^{13}C coupling constant in methyl cyclohexane is 3.72 Hz, which is 0.55 Hz less than the butane value in Table V. Although there is no experimental coupling-constant data for methylcyclohexane, a value of 3.2 Hz was reported for *cis*-4-*tert*-butyl-1-methylcyclohexanol (**12**).[2b,3] If it is assumed that the *tert*-butyl group effectively "locks" the ring into the conformation **12**, then this corresponds to a dihedral angle of 180°. The calculated result for $^3J_{CC'}(180°)$ in 2-butanol was found to be 3.82 Hz,[2,3] which was 0.6 Hz greater than the experimental value in **12**. It seems

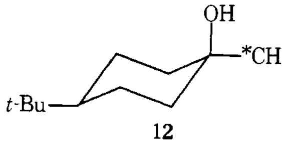


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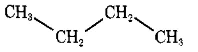
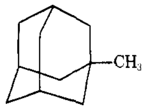
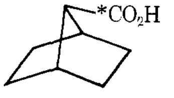
Table V. Calculated INDO-FPT Results for ${}^3J_{CC'}$ (180°) in Butane, Methylcyclohexane, and 1-Methyladamantane

Molecule	${}^3J_{CC'}$ (180°), Hz
	4.27
	3.72
	3.32

likely that the impinging of the multiple rear lobes would have the effect of decreasing the coupling constant in **12** by approximately the same amount as the difference (0.55 Hz) between the butane and methylcyclohexane values. The calculated and experimental results would be within the experimental error.

The calculated value of ${}^3J_{CC'}$ for 1-methyladamantane in Table V is 3.32 Hz, which is probably within the accuracy of the measurement of the 3.2 Hz experimental value in Table I. It is also just about 1 Hz less than the calculated butane value as well as the experimental values for the substituted butanes in Table I.

The effects of the impinging of multiple rear lobes also accounts for the apparent anomaly in previous results in the carboxylic acid series.[2a] In a study of vicinal ${}^{13}C-{}^{13}C$ coupling constants in a series of aliphatic and alicyclic carboxylic acids the maximum in the curve of ${}^3J_{CC'}(\phi)$ vs. ϕ appeared at an angle smaller than 180°. A maximum of 5.6 Hz was obtained for the norbornane carboxylic acid (**13**). This drops to 4.0 Hz in cyclohexanecarboxylic acid (**14**) and 4.2 Hz in 2-adamantanecarboxylic acid (**15**) and to 3.6 Hz in 1-adamantanecarboxylic acid (**16**).[2a] The decrease in this series due to the increasing number of impinging rear lobes is qualitatively consistent with the results in Table V, but the greater effect must be associated with hybridization and/or substituent effects of the carboxyl group.



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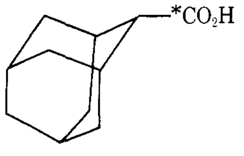

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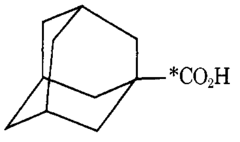

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III. Conclusions

The experimental values of vicinal ${}^{13}C-{}^{13}C$ coupling constants in substituted butanes are 1.2–1.4 Hz greater in magnitude than those in the similarly substituted 1-methyladamantanes. The effects of C1 substitution are relatively small and are presumably due to a combination of direct electronic perturbations of the coupling paths and substituent induced changes in rotamer populations.

By means of the VB bond-order formulation an expression was obtained which relates ${}^3J_{CC'}(\phi)$ to ${}^3J_{HH'}(\phi)$ as well as a number of angularly dependent long-range interproton coupling constants over four and five bonds. It is these long-range terms which lead to the much greater complexity for ${}^{13}C-{}^{13}C$ coupling than for the analogous H–H coupling. For example, a contribution of negative sign occurs for the all-trans arrangement of butane and it is interpreted as having its origin in the interactions between the "rear lobes" of the carbon hybrid orbitals. This is completely analogous to the mechanism which lead to long-range H–H coupling over four bonds in the "W" arrangement of a propanic fragment, but it is of opposite sign according to the VB formulation of eq 8. The greater values of ${}^{13}C-{}^{13}C$ coupling constants near the cis arrangements of butane are due to a combination of rather complicated direct interactions involving not only the atomic orbitals on the C1 and C4 carbon atoms, but also the bonded hydrogen atoms which are in close proximity.

In symmetrical molecules, such as the chair form of cyclohexane and adamantane, the higher symmetry presents the possibility for the impinging of several rear lobes. The VB bond-order formulation indicates that these should lead to negative and approximately additive contributions to ${}^3J_{CC'}$ (180°). This is consistent with the calculated INDO-FPT-MO results for the series butane, methylcyclohexane, and 1-methyladamantane (4.27, 3.72, and 3.32 Hz, respectively). The calculated value for methyladamantane is in good agreement with the experimental value of 3.2 Hz. Furthermore, the decrease of the coupling constants in this series, which follows the trend of increasing numbers of impinging rear lobes, removes several apparent anomalies in previous studies of the conformational dependencies of vicinal ${}^{13}C-{}^{13}C$ coupling constants. Furthermore, it is reasonable to expect that other types of coupling constants over two, three, and four bonds in these highly symmetric molecules will also be affected by the impinging rear lobes.

This study also reaffirms the fairly high reliability of the INDO-FPT computational scheme for studies of ${}^{13}C-{}^{13}C$ coupling constants in the aliphatic and alicyclic series. More importantly, it emphasizes that many other factors than dihedral angle are important for vicinal coupling and that extreme caution should be exercised in using the experimental data to estimate dihedral angles.

Experimental Section

Carbon NMR spectra were recorded on a Bruker-WH-90 Fourier transform NMR spectrometer operating at 22.63 MHz. Solutions of **1–11** were prepared in acetone-d_6, which served as an internal ${}^2H$ lock. The J_{CC} values were obtained using 8K/4K data points over a 600-Hz spectral width. Chemical-shift assignments for **1–6** were trivial and/or available from the literature.[30] Chemical-shift assignments for the adamantyl compounds **7–11** were made from structurally similar 1-substituted adamantane compounds.[31] For those compounds whose carbon-13 chemical shifts have not previously appeared in the literature, these values are included in Table I.

Synthesis of ${}^{13}C$-labeled compounds with an isotopic enrichment of >90% utilized carbon dioxide-${}^{13}C$ (Monsanto Corp., Miamisburg, Ohio) with vacuum-line techniques previously reported.[2a]

1-Butanol-*1*-${}^{13}C$ (1).[32] To a stirring slurry of 1.7 g of lithium aluminum hydride in 50 ml of anhydrous ether cooled to 0 °C was added over 45 min a solution of 3.83 g of butanoic acid-*1*-${}^{13}C$[2a] in 60 ml of anhydrous ether. The mixture was allowed to stir at room temperature for 3 days, cooled to 0 °C, and 6.9 ml of water was added dropwise. After 1 h of stirring, the mixture was filtered and the filtrate was concentrated by distillation to give 3.1 g of **1** (95%).

1-Cyanobutane-*1*-${}^{13}C$ (2).[33] A solution of 4.21 g of **5**, 2.28 g of potassium cyanide, and 25 ml of ethylene glycol was heated at reflux for 20 h. The solution was then distilled to give 2.14 g of **2** (75%), bp 130–140 °C.

1-Fluorobutane-*1*-${}^{13}C$ (3).[34] A mixture of 8.0 g of **6**, 10.9 g of mercuric fluoride, and 15 ml of chloroform was heated at reflux under argon for 15 min. Distillation (45–55 °C) then gave 1.5 g of **3** (45%).

1-Chlorobutane-*1*-${}^{13}C$ (4). The published procedure[35] for the synthesis of unlabeled **4** was carried out to give 2.31 g (82%) of labeled **4**.

1-Bromobutane-*1*-${}^{13}C$ (5). A solution of 3.4 g of **1**, 7.5 ml of 45% hydrobromic acid, and 3.7 ml of concentrated sulfuric acid was heated at reflux for 4 h. The mixture was distilled and the distillate collected at 70–120 °C was extracted with ether. The ethereal extract was dried (magnesium sulfate) and concentrated by distillation to give 5.2 g of **5** (83%).

1-Iodobutane-*1*-^{13}C (6). A solution of 3.2 g of **1** and 25 ml of 47% hydroiodic acid was heated at reflux for 12 h, cooled, and extracted with ether. The ethereal extract was dried (magnesium sulfate) and concentrated by distillation to give 7.7 g of **6** (95%).

1-Methyladamantane-*11*-^{13}C (7) was generously furnished by Dr. E. W. Della of the Flinders University of South Australia and Dr. D. M. Doddrell of Griffith University, Brisbane.

1-Hydroxymethyladamantane-*11*-^{13}C (8) was synthesized by reducing 1-adamantanecarboxylic acid-*11*-^{13}C[2a] in a manner as for **1** to give 3.0 g of **8** (86%), mp (methanol) 114–115 °C (lit.[36] mp 115 °C).

1-Cyanomethyladamantane-*11*-^{13}C (9).[37] A stirring slurry of 0.69 g of **11**, 0.2 g of potassium cyanide, and 10 ml of dimethyl sulfoxide was heated at reflux for 2 h, cooled, mixed with 20 ml of water, and extracted with ether. The ethereal extracts were dried (magnesium sulfate) and concentrated in vacuo to give 0.41 g of **9** (93%), mp (methanol) 73–74 °C (lit.[38] mp 73–74 °C).

1-Chloromethyladamantane-*11*-^{13}C (10).[39] A solution of 1.27 g of **8**, 5 ml of acetyl chloride, and 10 ml of dry ether was heated at reflux for 50 min and concentrated by distillation to give 1.30 g of **10** (92%), a colorless oil.[40]

1-Iodomethyladamantane-*11*-^{13}C (11). A mixture of 0.76 g of **8** and 3.5 ml of 47% hydroiodic acid was heated at reflux for 16 h, cooled, and extracted with ether. The ethereal extracts were washed with sodium bisulfite solution, dried (magnesium sulfate), and concentrated in vacuo to give 1.03 g of **11** (81%), mp 49–52 °C; recrystallization (methanol) gave white crystals, mp 51–52 °C.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the partial support of this research (to M.B.). Services of the University of Arizona computer center are gratefully acknowledged. This research was supported in part by the Robert A. Welch Foundation, Grant B-325, and the North Texas State University Faculty Research (to J.L.M.).

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