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Experimental and Theoretical Studies of ^{13}C–^{13}C Coupling Constants. 1. Conformational and Substituent Dependencies of Long Range Coupling Constants $^4J(^{13}C$–$^{13}C)$

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Abstract: The series of ^{13}C-labeled 1- and 2-substituted adamantanes and 2-substituted bornanes were synthesized, and their ^{13}C NMR parameters were accurately measured. Of particular interest in this study are the long range intercarbon coupling constants over four saturated bonds $^4J(^{13}C$–C–C–C–$^{13}C)$ as these have not previously been investigated. Depending on conformational and substituent factors, these coupling constants have magnitudes ranging from 0.1 to 0.73 Hz in the compounds investigated. Because of their relatively small values, the *J*-resolved technique of two-dimensional Fourier transform NMR was important for many of the measurements. In contrast to interproton coupling constants over four saturated bonds, $^4J_{HH'}$, the maximum values of $^4J_{CC'}$ are obtained in those conformations in which the coupled atoms are in closest proximity, rather than in the all-trans arrangements for which the $^4J_{CC'}$ are 0.3–0.6 Hz. Calculated results for the Fermi contact contributions to $^4J_{CC'}$, which were based on the INDO-FPT molecular orbital method, are in exceedingly good agreement with the experimental values. As a consequence, it appears that the computational methods improve as the coupled atoms are further separated, and that the long range coupling constants will be useful for spectral assignments.

Because of their relatively small magnitudes (usually less than 0.6 Hz), there are only a few examples in the literature[2–4] of long range ^{13}C–^{13}C coupling constants between carbon atoms separated by four or more aliphatic bonds. The use of the *J*-resolved techniques of two-dimensional Fourier transform NMR permits the accurate measurement of small coupling constants.[5,6] Furthermore, a major limitation associated with the requirements of ^{13}C labeling appears to have been removed by the introduction of double quantum coherence techniques,[7,8] which permit the measurement of small coupling constants in natural abundance samples. However, because of the abundance of information in the resulting spectra, some additional criteria may be required to assign the coupling constants correctly (e.g., in ref 7 it was incorrectly assumed that $|^4J_{CC'}| < |^2J_{CC'}|$). As a consequence, it will be of interest for such assignments to have information about the conformational and substituent factors for vicinal, geminal, and long range ^{13}C–^{13}C coupling constants. Vicinal ^{13}C–^{13}C coupling constants $^3J_{CC'}$ have been the subject of a large number of studies from these and other laboratories,[2–4,9–18] and are often larger in magnitude than $^2J_{CC'}$ and $^4J_{CC'}$. An experimental and theoretical study of geminal ^{13}C–^{13}C coupling $^2J_{CC'}$ will be the subject of the second paper in this series.[19]

Table I. Calculated INDO-FPT MO Results for $^4J_{CC'}$ in Pentane, 1-Pentanol, and Pentanoic Acid as a Function of the Dihedral Angles ϕ_1 and ϕ_2 [a]

		$^4J_{CC'}$, Hz		
ϕ_1, deg	ϕ_2, deg	pentane[b]	1-pentanol	pentanoic acid
0	60	20.82	20.83	17.71
0	180	0.46	0.46	−0.47
60	0	20.82	20.39	260.33
60	60	−0.05	−0.67	−0.16
60	180	−0.01	−0.06	−0.17
180	0	0.46	0.60	0.81
180	60	−0.01	−0.01	0.05
180	180	0.16	0.30	0.25
300	0	20.82	20.39	−1.14
300	60	19.81	19.66	−1.45
300	180	−0.01	−0.06	−0.23

[a] For the definition of the dihedral angles ϕ_1 and ϕ_2, see Figure 1. [b] In Figure 2, $^4J_{CC'}$ for pentane is plotted as a function of ϕ_1 and ϕ_2.

Because the conformational and substituent dependencies of long range ^1H–^1H coupling constants over four bonds have been reasonably well characterized,[20,21] it seems reasonable to examine the similarities to ^{13}C–^{13}C coupling over four bonds; the extension of the argument from $^4J_{HH'}$ in propane to $^4J_{CC'}$ in pentane suggests that the latter will depend on the dihedral angles ϕ_1 and ϕ_2 as depicted in Figure 1. The most conspicuous feature of $^4J_{HH'}$ in propanic systems is the large, positive maximum for the all-trans arrangement of the protons in which both dihedral angles are 180°. For other orientations the ^1H–^1H coupling constants tend to be much smaller in magnitude, and the resulting signs are probably determined by a combination of conformational and substituent effects. Substituents at the C2 carbon of propane produce shifts

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Table II. Comparisons of Calculated and Experimental Results for Long Range ^{13}C–^{13}C Coupling Constants in the 1-Substituted Adamantanes **2**, the 2-Substituted Adamantanes **4**, and the 1-Substituted 3,5-Dimethyladamantanes **3**[a]

	1-substituted adamantanes 2		2-substituted adamantanes 4					
	^4J(C4,C11)[b]		^4J(C5,C11)[c]		^4J(C7,C11)[b]		^5J(C6,C11)	
substituent	exptl	calcd	exptl	calcd	exptl	calcd	exptl	calcd
a, R = CH_3	(−)0.48	−0.44	(−)0.19	−0.16	(−)0.35	−0.34	0.17	0.12
b, R = CH_2OH	(−)0.55	−0.48	(−)0.13	−0.19	(−)0.35	−0.39	<0.13	0.12
c, R = CO_2H	(−)0.51	−0.58	<0.3	−0.25	(−)0.5	−0.54	<0.2	0.09
d, R = CH_2I	(−)0.55	*d*						
e, R = CH_2CN	(−)0.53	−0.46						
f, R = CO_2CH_3	*e*	*d*	0.2	−0.25	(−)0.42	−0.54	<0.2	0.09

	1-substituted 3,5-dimethyladamantanes 3b and 3c					
	^4J(C4,C11)		^4J(C6,C11)		^4J(C11,C12)[f]	
substituent	exptl	calcd	exptl	calcd	exptl	calcd
b, R = CH_2OH	(−)0.46	*d*	(−)0.45		<0.3	
c, R = CO_2H	(−)0.54	−0.61	(−)0.45	−0.61	0.29	0.58

[a] All values in hertz. The carbon atoms are numbered in the structural formulas. [b] Long range ^{13}C–^{13}C coupling occurs via dual paths each having $\phi_1 = 180°$ and $\phi_2 = 60°$. [c] Long range ^{13}C–^{13}C coupling occurs via dual paths each having $\phi_1 = 60°$ and $\phi_2 = 60°$. [d] Calculations were not performed for this molecule. [e] This value was not measured in this compound. [f] Long range ^{13}C–^{13}C coupling in the trans arrangement with $\phi_1 = \phi_2 = 180°$.

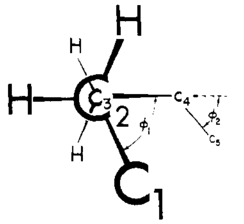

Figure 1. Specification of the dihedral angles ϕ_1 and ϕ_2 in the pentane moiety. These angles are measured in the same sense from the C2–C3–C4 plane.

of $^4J_{HH'}$ toward more positive values, but the same qualitative arguments lead to ambiguous results regarding the effects of substituents at C1 and C3. Therefore, by analogy substituents at the C3 carbon of pentane should lead to more positive values of $^4J_{CC'}$, but the effects of substituents at any of the other carbons will have to be inferred from the experimental results.

Results and Discussion

Conformational Dependencies of $^4J_{CC'}$ in Pentane, 1-Pentanol, and Pentanoic Acid. Calculated molecular orbital (MO) results were based on the finite perturbation theory (FPT) formulation in the semiempirical INDO (intermediate neglect of differential overlap) approximation of self-consistent-field (SCF) MO theory.[22-24] Molecular geometries for these molecules were based on the standard geometrical model (SGM) of Pople and Gordon,[25] but bond lengths and bond angles for the carboxyl group were based on data from the compilation of Sutton.[26] All calculations were performed on a Control Data Corp. CYBER 175 digital computer.

The calculated INDO-FPT MO results for pentane (**1a**), 1-pentanol (**1b**), and pentanoic acid (**1c**) are given in Table I for representative values of the dihedral angles ϕ_1 and ϕ_2. The dihedral angles are defined in Figure 1. Data from a more extensive set of calculated values are plotted in Figure 2 as a function of the two dihedral angles. From this figure and the data in Table I, it may be noted that the calculated values for dihedral angles near $\phi_1 = \phi_2 = 0°$ are exceedingly large. The values in Figure 2 have been truncated at +2 Hz to permit observation of some of the salient features of the angular dependence.

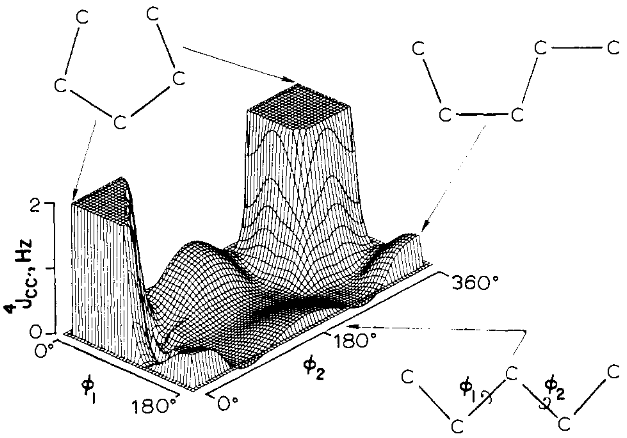

Figure 2. Calculated INDO-FPT MO results for $^4J_{CC'}$ in pentane plotted as a function of the dihedral angles ϕ_1 and ϕ_2. The calculated values were truncated at 2 Hz.

The enormous values of $^4J_{CC'}$ (0°,0°) do not correspond to any actual physical situation, since the energies are in excess of those required to distort the molecule. There is a relative maximum of +0.46 Hz corresponding to the "dipper" arrangement with $\phi_1 = 180°$ and $\phi_2 = 0°$. In marked contrast to the situation for $^4J_{HH'}$, a relative maximum of only 0.16 Hz is predicted for $^4J_{CC'}$ in the all-trans arrangement of pentane.

The calculated values for pentane and 1-pentanol indicate that nonbonded interactions involving the hydrogens on the C1 and C5 carbon atoms lead to large positive values of $^4J_{CC'}$. The conformation of 1-pentanol, which was used in the MO calculations, corresponds to 180° for the dihedral angle C3–C2–C1–O; if the OH group were directed toward the C5 methyl group, the calculated $^4J_{CC'}$ for ϕ_1 and ϕ_2 near 0° would be much reduced. A completely analogous trend was noted in vicinal ^{13}C–^{13}C coupling constants in a series of 1-substituted 2,2-dimethylcyclopropanes.[27] Furthermore, the $^4J_{CC'}$ for pentanoic acid near the all-cis arrangement are smaller because of the absence of the possibility for interactions between hydrogens.

Some trends to look for in the experimental data are as follows: The $^4J_{CC'}$ (180°,180°) may be increased by electronegative substituents on the C1 carbon as the calculated values for **1a**, **1b**, and **1c** are 0.16, 0.30, and 0.25 Hz, respectively. In the cases of **1b** and **1c**, there are two possible dipper arrangements; for $\phi_1 = 180°$

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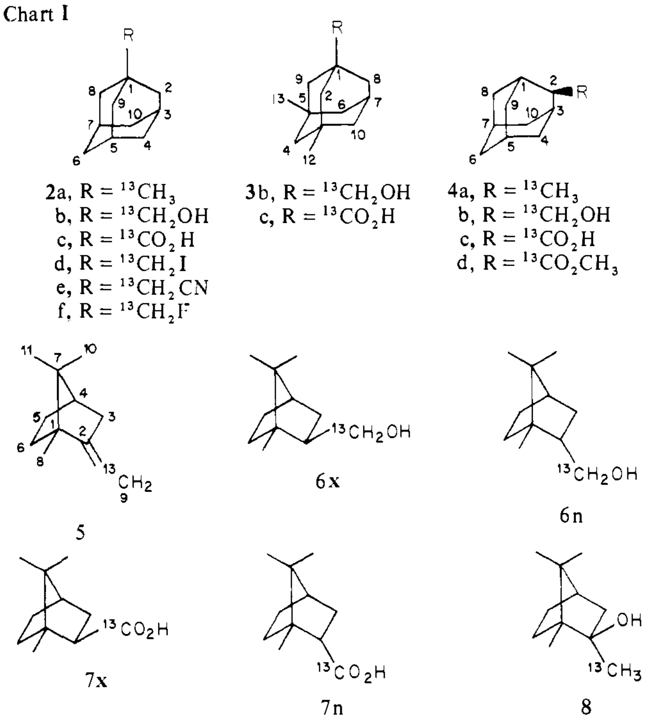
Table III. Comparisons of Calculated and Experimental Results for Long Range ^{13}C–^{13}C Coupling Constants in the 2-Substituted Bornanes 5–8[a]

	^4J(C5,C9)		^4J(C9,C10)		^4J(C9,C11)	
compound	exptl	calcd	exptl	calcd	exptl	calcd
5	0.29	*b*	<0.15	*b*	0.18	*b*
6x (R = CH_2OH)	(–)0.33[c]	–0.32	0.73[d]	–0.11	<0.11[e]	–0.13
6n (R = CH_2OH)	<0.15[f]	–0.18	<0.11[g]	0.07	0.33[h]	–0.05
7x (R = CO_2H)	(–)0.42[c]	–0.46	<0.11[d]	–0.44	<0.17[e]	–0.18
7n (R = CO_2H)	<0.18[f]	–0.24	<0.08[g]	–0.08	0.28[h]	0.08
8	<0.6[f]	*b*	<0.1[g]	*b*	0.51[h]	*b*

[a] All values in hertz. The numbering of the atoms is given in the structural formulas. [b] Calculations were not performed for this compound. [c] Dual coupling paths with $\phi_1 = 120°$, $\phi_2 = 70°$, $\phi_1' = 170°$, $\phi_2' = 70°$. [d] $\phi_1 = 277°$, $\phi_2 = 62°$. [e] $\phi_1 = 83°$, $\phi_2 = 175°$. [f] Dual coupling path with $\phi_1 = 52°$, $\phi_2 = 71°$, $\phi_1' = 237°$, $\phi_2' = 71°$. [g] $\phi_1 = 159°$, $\phi_2 = 62°$. [h] $\phi_1 = 201°$, $\phi_2 = 175°$.

Chart I



2a, R = $^{13}CH_3$
b, R = $^{13}CH_2OH$
c, R = $^{13}CO_2H$
d, R = $^{13}CH_2I$
e, R = $^{13}CH_2CN$
f, R = $^{13}CH_2F$

3b, R = $^{13}CH_2OH$
c, R = $^{13}CO_2H$

4a, R = $^{13}CH_3$
b, R = $^{13}CH_2OH$
c, R = $^{13}CO_2H$
d, R = $^{13}CO_2CH_3$

5

6x

6n

7x

7n

8

and $\phi_2 = 0°$ the calculated values of $^4J_{CC'}$ (180°,0°) for **1a**, **1b**, and **1c** are 0.46, 0.60, and 0.81 Hz, respectively. However, the values of $^4J_{CC'}$ (0°,180°) are decreased by the non-hydrogen substituents on the C1 carbon, which are directed toward the C4 carbon; the calculated values are 0.46, 0.46, and –0.47 Hz, respectively.

Comparison of Calculated and Experimental Results. Experimental values of $^4J_{CC'}$ in the series of substituted adamantanes **2**–**4**, and 2-substituted bornanes **2**–**8** from the Experimental Section are compiled in Tables II and III. The relevant dihedral angles are included in the footnotes of the two tables. A number of other values of long range ^{13}C–^{13}C coupling constants were also obtained in the course of the investigations. For example, all of the $^4J_{CC'}$ in eight 2-substituted fenchanes are less than 0.2–0.5 Hz.[17] None of the signs of these long range coupling constants have been determined; all values in parentheses are assumptions based on calculated results or trends in substituent effects. The assumed signs should be used with caution until confirmed experimentally. In the several examples wherein the calculated and experimental magnitudes were not in excellent agreement in the two tables, i.e., ^4J(C9,C10) and ^4J(C9,C11) and Table III, no signs were assumed. With the possible exception of the 0.73-Hz coupling in **6x**, the best that can be said is that the magnitudes are small in these compounds.

Also included in Table II are several results for intercarbon coupling ^5J(C6,C11) over five bonds along dual paths in the 2-substituted adamantanes. The only splitting was one of 0.17 Hz, which was noted in a *J*-resolved experiment for 2-methyladamantane. Since these $^5J_{CC'}$ correspond to coupling over four 5-bond paths, the physical situation is quite complicated and will not be discussed further.

Also included in Tables II and III are the calculated INDO-FPT MO results for the Fermi contact contributions. The geometries of the adamantane compounds were based on an SGM,[25] but the bicyclo[2.2.1]heptane framework for bornanes **5**–**8** was based on electron diffraction results.[28] In view of the approximations of the theoretical methods and uncertainties of the details of the molecular geometries, the calculated results for both $^4J_{CC'}$ and $^5J_{CC'}$ are in excellent agreement with the experimental data. In fact, most of the calculated results in Tables II and III are within the experimental errors of the measurements. Conspicuous exceptions are the underestimation and overestimation of ^4J(C9,C10) in **6x** and **7x**, respectively, and the overestimation of ^4J(C9,C11) in **6n** and **7n**.

The experimental results for the all-trans arrangements in **3b** and **3c** (also note the results for ^4J(C9,C11) in **6n**, **7n**, and **8**) clearly indicate that this is not the most important conformational feature for long range ^{13}C–^{13}C coupling. The largest magnitude for any long range ^{13}C–^{13}C coupling constant is 0.73 Hz between the exo hydroxymethyl carbon C9 and the methyl carbon C10 of the bornane **6x** in Table II. In this case the dihedral angles are 277° and 62°, which correspond to values for which large positive values for $^4J_{CC'}$ are expected from Figure 2. Furthermore, the long range coupling constant in the carboxylic acid **7x** was too small to be measured due to the absence of hydrogens on the α-carbon atom. The disparity between the calculated and experimental results for *J*(C9,C10) in **6x** may be a further indication of the inadequacy of the INDO-FPT MO method applied to long range coupling constants between proximate nuclei.[29]

A very interesting trend in the experimental data in Table II is the relative insensitivity of the $^4J_{CC'}$ to substituents at the terminal carbon. For example, note the data for the 1-substituted adamantanes **1a**–**e**. In these cases the conformations are such that nonbonded interactions between the atoms of the coupled nuclei would not be an important factor.

The only significant suggestion of a β-substituent effect (β-hydroxyl) is the approximately 0.2 Hz increase of ^4J(C9,C11) in 2-methylhydroxybornane (**8**) compared to the values in the 2-endo-substituted bornanes **6n** and **7n**. Factors other than changes in the two dihedral angles and α- and β-substituent factors are undoubtedly important for long range ^{13}C–^{13}C coupling constants. For example, the (–)0.33- and (–)0.42-Hz coupling constants in the 2-exo-substituted bornanes **6x** and **7x** are substantially larger than the coupling constants (<0.2 Hz) in the 2-exo-substituted fenchanes.[17] Since similar $^4J_{CC'}$ values are very small in the 2-endo-substituted bornanes and fenchanes, the larger values in **6n** and **7n** are probably caused by interactions between the *syn*-methyl group and the substituent atoms.

Conclusions

In contrast to long range coupling constants between protons separated by four bonds, long range intercarbon coupling constants

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Table IV. Carbon-13 NMR Data for the 1-Substituted Adamantanes 2a–f[a]

compd		C1	C2,C8,C9	C3,C5,C7	C4,C6,C10	C11
2a	$\delta^{b,c}$	29.75 (1)	44.68 (1)	28.91 (1)	36.97 (1)	31.43
	J	36.97 (7)	<0.2	3.26 (4)[d]	0.48 (4)	
2b	δ^{e}	34.7	39.4	28.4	37.5	73.2
	J	40.3 (1)	0.17	3.31 (2)[f]	0.55 (6)[f]	
2c	$\delta^{b,g}$	40.59 (3)	38.71 (3)	27.99 (3)	36.57 (3)	184.82 (3)
	J	56.60 (12)	1.39 (12)	3.20 (12)	0.4 (2)[h]	
2d	δ^{d}	32.35 (3)	42.11 (3)	28.74 (3)	36.67 (3)	26.26 (3)
	J	36.31 (7)	<0.2	3.68 (4)[d]	0.55 (4)	
2e	δ^{d}	*i*	41.87	28.44	36.44	32.3
	J	*i*	<0.07[f]	3.82 (15)[d]	0.53 (4)[f]	
2f[j]	δ	28.64 (3)	38.26 (3)	28.01 (3)	37.07 (3)	92.41
	J_{CF}	13.55 (7)	4.27 (7)	1.04 (7)	<0.8	172.8 (1)

[a] Dissolved in $CDCl_3$ unless noted otherwise. Chemical shifts δ are referenced to high frequency of internal Me_4Si and coupling constants J in hertz are between carbons unless noted otherwise. [b] δ values in CCl_4 were reported by Maciel et al., ref 43. [c] Less accurate values were reported by Pehk et al.: Pehk, T.; Lippmaa, E.; Sevostjanova, V. V.; Krayuschkin, M. M.; Tarasova, A. I. *Org. Magn. Reson.* 1971, *3*, 783. [d] Less accurate values were reported in ref 23. [e] Values reported by Pehk et al., footnote *c*. [f] Measured in a J-resolved NMR experiment. [g] Less accurate values were reported in tetrahydrofuran in ref 20. [h] A value of 0.51 (2) Hz was obtained in a J-resolved experiment with acetone-d_6 as solvent. [i] These values were not determined. [j] Values obtained in a mixture of 60% 2d and 40% 2f.

do not appear to depend so strongly on conformation. For example, single path values inferred from the data of Table II cover the very small range of 0.13–0.25 Hz. Moreover, this study suggests that only the all-cis conformations, such as the one leading to the 0.73-Hz value in **6x**, are likely to produce coupling constants greater than 0.6 Hz. In conformations near the all-cis arrangements, the C1- and C5-carbons are close enough to cause significant nonbonded coupling pathways involving the hydrogens of the terminal carbons.[27] Carbons in the all-trans arrangement produce 0.3–0.5-Hz long range coupling constants; these may prove large enough to differentiate carbons in this arrangement.

Calculated results appear to improve as the number of bonds separating the coupled atoms increases. However, important exceptions in both magnitude and sign are known to occur in those cases in which the coupled nuclei are proximate.[29]

Experimental Section

Synthesis. Carbon-13 labeled carbon monoxide and carbon dioxide (>90% isotopically enriched) were purchased from Prochem Chemical Co., B.O.C., Ltd., London SW19 3UF, U.K. 1-Bromoadamantane and 2-bromoadamantane were obtained from Aldrich Chemical Co., Milwaukee, WI. Melting points were determined on a Thomas–Hoover apparatus. Proton NMR spectra were recorded at 60 MHz on a Varian Associates EM-360 NMR spectrometer. Infrared spectra were recorded on a Beckman IR-33 infrared spectrometer. Mass spectra were recorded on a Hitachi Perkin-Elmer RMU-6E double-focussing mass spectrometer.

1-Adamantanecarboxylic acid-*11*-^{13}*C* (2c),[9] **1-(hydroxymethyl)adamantane-*11*-^{13}*C* (2b)**,[14] **1-(iodomethyl)adamantane-*11*-^{13}*C* (2d)**,[30] **1-(cyanomethyl)adamantane-*11*-^{13}*C* (2e)**,[12] **2-adamantanecarboxylic acid-*11*-^{13}*C* (4c)**,[9] **and 2-(hydroxymethyl)adamantane-*11*-^{13}*C* (4b)**[14] were prepared according to previously described procedures.[9,12,14,30]

1-Methyladamantane-*11*-^{13}*C* (2a). 1-(Iodomethyl)adamantane (**2d**) was converted to the Grignard derivative via activated magnesium as for the 2-isomer (vide infra) to give 90% (1.5 g) of 1-methyladamantane-*11*-^{13}*C*, purified by passing through alumina (Alcoa F-20) with hexane to give 1.4 g, mp 100–102 °C (lit.[31] mp 103 °C).

1-(Fluoromethyl)adamantane (2f). A mixture of 3.75 g of 1-(iodomethyl)adamantane (**2d**), 2.00 g of anhydrous potassium fluoride, and 2.54 g of 18-crown-6 was heated in a sealed glass ampule at 160 °C for 12 days, cooled, mixed with 100 mL of water, and extracted with two 50-mL portions of ether. The combined ethereal extracts were washed with 50 mL of brine, dried (anhydrous magnesium sulfate), and concentrated in vacuo to give a viscous syrup whose NMR indicated 60:40 composition of reactant:product. This 60:40 mixture was analyzed by ^{13}C NMR without further purification.

3,5-Dimethyl-1-adamantanecarboxylic Acid-*11*-^{13}*C* (3c). 1-Bromo-3,5-dimethyladamantane (5.2 g, Aldrich Chemical Co.) was converted to the carboxylic acid **3c** by using the usual carbonylation procedure[9] to give 4.22 g (94.4%) of product, mp 105–106 °C (lit.[32] mp 106.5–107.5 °C).

Table V. Carbon-13 NMR Parameters for 1-Substituted 3,5-Dimethyladamantanes 3b and 3c[a]

	3b		3c	
carbon	δ	J	δ	J
C1	36.90 (3)	39.71 (15)	42.59	57.36 (7)
C2, C9	46.13 (3)	<0.08[b]	45.48	1.40 (7)
C3, C5	31.31 (3)	3.39 (3)	31.24	3.37 (7)
C4	51.98 (3)	0.46 (4)[b]	51.17	0.54 (6)[b]
C6, C10	44.05 (3)	0.45 (3)[b]	43.27	0.45 (5)[b]
C7	30.06 (3)	3.52 (3)	29.79	3.51 (7)
C8	38.36 (3)	<0.09[b]	38.00	1.37 (5)
C11	72.79 (3)		180.23	
C12, C13	31.02 (3)	<0.3[b]	30.72	0.29 (4)[b]

[a] Chemical shifts in ppm downfield from Me_4Si; coupling constants in hertz; acetone-d_6 as solvent. [b] Measured in J-resolved experiments.

1-(Hydroxymethyl)-3,5-dimethyladamantane-*11*-^{13}*C* (3b). The carboxylic acid was reduced with lithium aluminum hydride in the usual manner[14] to give 1.0 g (75%) of **3b**, mp 50–51 °C (lit.[33] mp 55–56 °C).

2-Methyladamantane-*11*-^{13}*C* (4a) was synthesized by conversion of the alcohol **4b** to the chloride, conversion to the Grignard reagent by using activated magnesium, and hydrolysis (reduction of the chloride with lithium aluminum hydride gave inferior yields). A solution of 2-(hydroxymethyl)adamantane-*11*-^{13}*C* (5.08 g, **4b**), 5 mL of thionyl chloride, and 100 mL of dry ($BaSO_4$) pyridine was stirred under reflux for 12 h. Then 100 mL of 12 N hydrochloric acid was added. The mixture was extracted with three 100-mL portions of ether. The combined ether extracts were dried (anhydrous magnesium sulfate), concentrated in vacuo, and distilled trap-to-trap to give 1.9 g (26%) of the chloride, a pale yellow liquid. The chloride in 25 mL of dry tetrahydrofuran was added dropwise to a stirring mixture of activated magnesium in tetrahydrofuran (produced by mixing and then refluxing for 2.5 h a mixture of 1.19 g of anhydrous magnesium chloride, 1.66 g of freshly cut potassium metal, and 150 mL of dry tetrahydrofuran). The resulting mixture was stirred under reflux for 12 h, quenched with water, and extracted with three 100-mL portions of ether. The combined ethereal extracts were dried (anhydrous magnesium sulfate), concentrated in vacuo, and purified by passing through a column of alumina (Alcoa F-20) with hexane and subsequent sublimation to give 1.3 g (87% yield based on chloride) of a sticky white solid, mp 132 °C (lit.[34] mp 143.8–146 °C).

2-(Carboxymethyl)adamantane-*11*-^{13}*C* (4g). 2-Adamantanecarboxylic acid-*11*-^{13}*C* (2.0 g) in 100 mL of pentane was treated with 1.3 g of thionyl chloride in 25 mL of benzene. The resulting solution was refluxed overnight, cooled, quenched with 5 mL of methanol, stirred for 12 h, washed with 5% aqueous sodium bicarbonate solution and 100 mL of water, dried (anhydrous magnesium sulfate), and concentrated in vacuo to give white crystals, mp 30–35 °C (lit.[35] mp 39–39.5 °C).

Methyl-^{13}*C* Iodide. To 250 mL of dry tetrahydrofuran in a 500-mL round-bottom flask, 10.5 g of lithium aluminum hydride was added. This

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Table VI. Carbon-13 NMR Parameters for 2-Substituted Adamantanes 4a–c,g

compd		C1, C3	C2	C4, C9	C5	C6	C7	C8, C10	C11	C12
4a[a]	δ[b]	33.92	39.18	31.44	28.61	38.75	28.28	39.57	18.95	
	J	0.60 (2)[c]	0.60 (2)	35.8 (1)	0.91 (2)[c]	0.19 (2)[c]	0.17 (3)[c]	0.35 (2)[c]	3.42 (6)	
4b[a]	δ[d]	29.36 (3)	46.99 (3)	32.06 (3)	28.16 (3)	38.37 (3)	25.58 (3)	39.10 (3)	64.67 (3)	
	J	0.27 (3)[c,d]	38.3 (7)[d]	0.85 (16)	0.13 (4)[c]	0.13	0.35 (3)[c]	3.59 (16)[d]		
4c[e]	δ[f]	29.77 (1)	49.75 (1)	33.83 (1)	27.85 (1)[g]	37.59 (1)	27.85 (1)[g]	38.23 (1)	181.54 (9)	
	J	1.09 (5)	56.98 (10)	0.37 (5)	<0.3	<0.2	0.5 (2)	4.44 (2)		
4g[e]	δ	29.99 (1)	49.78 (1)	33.86 (1)	27.96 (1)[h]	37.71 (1)	27.96 (1)[h]	38.36 (1)	174.36 (9)	50.91 (1)
	J	1.21 (2)	54.48 (9)	0.40 (2)	<0.2	<0.2	0.42 (5)	4.51 (2)		2.74

[a] Measured in chloroform-*d* solvent. [b] Chemical shifts were reported in CCl_4/C_5H_{10} (ref 43); in $CDCl_3$ (ref 18 and 41); Maciel et al.[43] had C5 and C7 incorrectly reversed, and Barfield et al. reported the assignments of C5 and C7 as uncertain[18] and they are incorrectly reversed. Also, C1 and C4 are reversed.[18] [c] Measured in a *J*-resolved experiment. [d] Less accurate values were reported by Barfield, Marshall, and Canada, footnote *b*. [e] Measured in benzene-d_6 solvent. [f] The assignments agree with those in ref 9. The assignments of C6 and C8 are reversed in ref 43. [g] On the WM-250 NMR C7 is 0.2 Hz (0.003 ppm) upfield of C5; these were assigned by using the $^4J_{CC'}$. [h] On the WM-250 NMR C5 is 0.5 Hz (0.008 ppm) upfield of C7; these were assigned on the basis of the four-bond coupling constants.

flask was then attached to a previously calibrated vacuum manifold[9] and vacuum degassed. The mixture was cooled to −30 °C by using a 6:1 methanol:water slush. Next, eight successive 1.0-g volumes of ^{13}C-labeled carbon dioxide were expanded into the manifold and allowed to react with the hydride slurry. The mixture was then allowed to warm to room temperature and stirred overnight. The reaction was then removed from the vacuum line, treated with 222 mL of benzyl alcohol, stirred for 4 h, and distilled through a 10-cm vacuum-jacketed column to remove the tetrahydrofuran and methanol. This distillate was treated with 11 g of metallic sodium and allowed to reflux for 48 h. The unreacted sodium was removed and the solution was distilled to leave the sodium methoxide residue. This product was not isolated but was converted to methyl iodide by treatment with 1.8 g of ice and 250 mL of 55% hydroiodic acid. Distillation gave a quantitative yield, bp 42–43 °C, proven by ^1H NMR and GLC to be 99% methyl iodide.

Methyl-^{13}*C*-triphenylphosphonium Iodide. To a mixture of 55 g of triphenylphosphine (Aldrich Chemical Co.) in 60 mL of benzene, cooled in an ice bath and under an argon atmosphere, was added 40 g of methyl-^{13}*C* iodide. This mixture was allowed to stand at ambient temperature overnight. The resulting white solid was washed twice with benzene and dried at 80 °C for 32 h to give a quantitative yield of the product.

Methyl-^{13}*C*-magnesium Iodide. A flask purged with argon was charged with 1 g of Grignard grade magnesium turnings and a single small crystal of iodine. The flask was heated until iodine vapor was detected and then cooled. Next, 50 mL of anhydrous ether followed by 0.5 g of methyl-^{13}*C* iodide were added. After evidence that the reacton had begun was observed, 3.5 g of methyl-^{13}*C* iodide in 50 mL of anhydrous ether was added over a 4-h period. The resulting Grignard solution was either used in situ or transferred by using syringe techniques, as required in the next synthetic step.

Methyl-^{13}*C*-lithium. Lithium sand was prepared by shaking a hot flask of molten lithium in mineral oil and hexane under argon, cooling, and washing with anhydrous ether. A solution of methyl-^{13}*C*-lithium was prepared by refluxing for 1 h under argon a mixture of 6 g of lithium sand, 10.5 g of methyl-^{13}*C* iodide, and 25 mL of anhydrous ether.

1,7,7-Trimethyl-2-methylene-^{13}*C*-bicyclo[2.2.1]heptane (2-Methylene-^{13}*C*-bornane) (5).[36] A mixture of 12 g (0.5 mol) of sodium hydride in 100 mL of dry dimethyl sulfoxide was heated at 50 °C for 1 h, cooled in an ice bath, and treated with 20.0 g (0.05 mol) of methyl-^{13}*C*-triphenylphosphonium iodide in 50 mL of dimethyl sulfoxide (all under an argon atmosphere). The resulting dark red solution of the yield was warmed to room temperature, stirred for 10 min, treated with 6.0 g of (+)-camphor in 10 mL of dimethyl sulfoxide, heated at 50 °C overnight, cooled, poured into 300 mL of pentane, and washed with four 50-mL portions of water. The combined water washings were extracted with four 50-mL portions of pentane. The combined organic fractions were washed with six 100-mL portions of brine, dried (anhydrous magnesium sulfate), and distilled to give a thick oil residue. Chromatography of this oil with use of pentane with F-20 alumina gave, upon removal of solvent, 4.5 g (75%) of product, mp 65 °C (lit.[36] mp 68 °C): IR (KBr) cm^{-1} 3200–2800, 1675, 1490, 900; ^1H NMR ($CDCl_3$) δ 4.6 (d, 2 H, system additionally split *J* = 150 Hz), 2.5–1.1 (complex, 7 H), 0.92 (s, 3 H), 0.90 (s, 3 H), 0.78 (s, 3 H); mass spectrum *m/e* (for ^{13}C labeled) M 151, 136, 122, B 108.

1,7,7-Trimethyl-2-bicyclo[2.2.1]heptanemethanol-^{13}*C* (2-Bornylcarbinol-^{13}*C*) (6) via Hydroboration. Hydroboration of **5** by using the procedure of Brown[37] gave 2.0 g (85%) of clear oil which proved by NMR analysis to be a 76:24 ratio of exo:endo isomers: IR (neat) 3400, 2950, 1475, 1375 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.6 (m 2 H, system additionally split *J* = 137 Hz), 3.0 (s, 1 H, exchangeable), 2.0–1.0 (complex, 8 H), 0.86 (s, 6 H), 0.83 (s, 3 H); mass spectrum (for ^{13}C-labeled) M 169, 151, B 95.

Table VII. Carbon-13 NMR Parameters for the 2-Substituted Bornanes 5, 6n, and 6x

carbon	5[a,b]		6n[c]		6x[c]	
	δ[a]	J	δ	J	δ	J
C1	51.54 (1)	1.39 (4)	47.59	<0.05	47.67[d]	<0.16
C2	159.49 (3)	74.30 (7)	46.59	40.11 (5)	51.32	38.57 (5)
C3	37.14 (1)	1.43 (4)	34.89	0.81 (4)	35.09	0.70 (4)
C4	44.99 (1)	2.82 (4)	45.98	1.26 (4)	45.98	1.39 (4)
C5	28.13 (1)	0.29 (4)	27.37	<0.15	27.96	0.33 (4)
C6	35.34 (1)	2.31 (4)	29.46	3.81 (4)	40.58	3.37 (5)
C7	47.30 (1)	2.16 (4)	49.70	2.69 (5)	47.37[d]	0.15 (2)
C8	12.49 (1)	2.38 (4)	15.28	<0.18	13.03	2.38 (4)
C9	101.33 (3)		65.13		66.39	
C10	19.75 (1)	<0.15	18.88	<0.11	20.91	0.73 (4)
C11	19.00 (1)	0.18 (4)	19.34	0.33 (4)	20.90	<0.11

[a] Chemical shift values for C8, C10, and C11 were reported by Grover and Stothers: Grover, S. H.; Stothers, J. B. *Can. J. Chem.* 1975, *53*, 589. [b] Measured in $CDCl_3$ solvent. [c] Measured in acetone-d_6 solvent. [d] The assignments for C1 and C7 may be reversed.

1,7,7-Trimethyl-2-bicyclo[2.2.1]heptanecarboxylic-^{13}*C* Acid (2-Bornanecarboxylic-^{13}*C* Acid) (7) via Oxidation of the Alcohol 6. Oxidation of **6** (1.0 g) in 20 mL of acetone with 1 g of chromium trioxide, 1 mL of concentrated sulfuric acid, and 15 mL of water at room temperature for 1 h gave after workup (extraction with four 50-mL portions of ether, combination of the ethereal extracts, drying with anhydrous magnesium sulfate, and concentration in vacuo) a clear oil which proved by NMR analysis to be a 49:51 mixture of exo:endo isomers of **7**[38] (epimerization occurs during oxidation and a mild procedure is necessary): IR (KBr) 3600–2600, 1725 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.0 (s, 1 H, exchangeable), 2.2–0.9 (complex, 8 H); 1.0 (s, 3 H), 0.9 (s, 6 H); mass spectrum *m/e* (for ^{13}C-labeled compound) M 183, 139, 110, 95.

1,7,7-Trimethyl-2-bicyclo[2.2.1]heptanecarboxylic-^{13}*C* Acid (2-Bornanecarboxylic-^{13}*C* Acid) (7) via Carbonation of the Grignard Reagent. Carbonation[9] of 2-bornyl Grignard reagent with carbon-^{13}C dioxide gave the endo-carboxylic acid **7n** in 78% yield. To obtain good yields of **7n** on the basis of carbon dioxide, Grignard reagents via activated magnesium were made. Activated magnesium was prepared by the following procedure: A three-neck flask was charged with 2.7 g of magnesium shavings, 0.5 g of iodine, and 21.5 g of amyl chloride under an argon atmosphere. With gentle heating, the reaction was complete in 2 h, and yielded anhydrous magnesium chloride and decane. The decane was removed by washing the solid with dry pentane (**Caution**: the anhydrous magnesium chloride is pyrophoric). Then 10 mL of anhydrous tetrahydrofuran (exothermic reaction) and 7.2 g of potassium metal cut into small pieces were added and the mixture was brought to reflux while being stirred. The resulting gray-black dispersion of magnesium was stirred until no further potassium was present in the mixture. The desired Grignard reagent was formed rapidly by adding the appropriate halide with stirring and cooling.

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Table VIII. Carbon-13 NMR Parameters for the 2-Substituted Bornanes 7n, 7x, and 8

	7n[a]		7x[a]		8[a]	
carbon	δ	J	δ	J	δ	J
C1	49.88 (1)	1.25 (4)	50.14 (1)	0.92 (4)	52.15 (2)	1.39
C2	50.24 (1)	57.67 (4)	51.71 (1)	56.02 (4)	78.59 (2)	40.70 (19)
C3	32.01 (1)	<0.2	33.07 (1)	1.44 (5)	48.21 (2)	2.54 (8)
C4	45.97 (1)	1.43 (4)	46.12 (1)	1.41 (4)	46.09 (2)	1.36 (8)
C5	28.36 (1)	<0.2	28.17 (1)	0.42 (5)	31.42 (2)	<0.6
C6	31.11 (1)	2.17 (5)	40.21 (1)	4.54 (3)	31.64 (2)	3.08 (11)
C7	50.29 (1)	4.25 (4)	48.42 (1)	<0.18	49.32 (2)	1.75 (8)
C8	14.59 (1)	<0.26	15.32 (1)	0.84 (4)	10.33 (2)	<0.4
C9	176.95 (1)		176.68 (1)		27.13 (2)	
C10	19.12 (1)	<0.11	19.92 (1)[b]	<0.11	21.93 (2)	<0.1[c]
C11	19.52 (1)	0.31 (2)	20.60 (1)[b]	<0.17	21.49 (2)	0.51 (2)[c]

[a] Measured in acetone-d_6 solvent. [b] The assignments for C10 and C11 may be reversed. [c] Measured in a J-resolved experiment.

1,7,7-Trimethyl-*endo*-2-bicyclo[2.2.1]heptanemethanol-^{13}C (*endo*-2-Bornylcarbinol-^{13}C) (6n) via Reduction of the Carboxylic Acid 7. Lithium aluminum hydride reduction of **7** in the usual manner[14] gave 1.8 g (82%) of **6n**, mp 74–75 °C (lit.[38] mp of + mixture 77.5–79 °C).

1,2,7,7-Tetramethylbicyclo[2.2.1]heptan-*exo*-2-ol-*9*-^{13}C (*exo*-2-Methyl-^{13}C-bornyl Alcohol) (8). (+)-Camphor (5.0 g) in 50 mL of anhydrous ether under an argon atmosphere, cooled in an ice bath, was treated with methyl-^{13}C-lithium in 30 mL of anhydrous ether by syringe. The resulting mixture was stirred overnight, treated with 1 mL of water and sufficient 6 N hydrochloric acid to render the mixture acidic, and extracted with three 50-mL portions of ether. The combined ethereal extracts were dried (anhydrous magnesium sulfate) and concentrated in vacuo to give 4.9 g of a solid. Residual camphor was removed by chemical separation as the oxime as follows: The solid was taken up in 50 mL of 95% ethanol, treated with 5 g of potassium hydroxide followed by 3 g of hydroxylamine hydrochloride, and heated under reflux for 48 h; the mixture was cooled and decanted from the crystals of the oxime which formed. The crystals were washed with 10 mL of pentane which were added to the supernatant liquid. The liquid mixture was mixed with 200 mL of pentane and washed with five 100-mL portions of 2 M potassium hydroxide solution and two 50-mL portions of brine. The organic layer was dried (anhydrous magnesium sulfate) and concentrated in vacuo to give 4.6 g of white semisolid (32% yield based on methyl iodide), mp 150–155 °C (lit.[39] mp 154–155 °C): ^{1}H NMR ($CDCl_3$) δ 2.2–1.2 (complex, 7 H), 1.1 (s, 3 H, system additionally split $J = 125$ Hz), 1.0 (s, 3 H), 0.92 (s, 6 H); mass spectrum m/e (for ^{13}C-labeled compound) M 183, 165, B 95.

Carbon-13 NMR Spectra. Carbon-13 NMR spectra were recorded at 22.63 and 62.86 MHz on Bruker Instruments WH-90 FT NMR and WM-250 superconducting FT NMR spectrometers, respectively. Either chloroform-d, acetone-d_6, or benzene-d_6 was used as solvent and internal ^{2}H lock material. Chemical shifts are referenced downfield from internal tetramethylsilane (Me_4Si). In all cases the digital resolution, as determined by spectral widths and computer memory size, was better than the estimated errors.

Many of the ^{13}C NMR spectra were obtained by the two-dimensional NMR techniques of J-resolved spectroscopy.[5,6] These were performed with NTCFT software[40] on an NIC-80/WH-90 spectrometer equipped with an NIC-293 pulse programmer. An assembly language computer program was written[2,41] to perform the transposition of the spectra. The 90°–τ–180° pulse sequence was used; typical spectra were obtained with 16 τ values ranging from 0.0 to 3.75 s. The resolution depends on the individual carbon T_2 values, but it was at least 0.12 Hz with an accuracy of at least 0.05 Hz. Some of the smaller splittings were also obtained on the WM-250 by using the technique of Gaussian multiplication for resolution enhancement.

1-Substituted Adamantanes (2a–f). The chemical shifts and ^{13}C–^{13}C coupling constants for the 1-substituted adamantanes are entered in Table IV. All of the existing assignments were confirmed by single-frequency off-resonance decoupling (SFORD) experiments. Since the assignments of C2(C8,C9) and C4(C6,C10) were crucial to these discussions, the ^{13}C NMR spectrum of 1-(fluoromethyl)adamantane (**2f**) was also examined and the results included in Table IV; the larger ^{13}C–^{19}F coupling of 4.27 Hz was assumed to be the three-bond one to C2, whereas the five-bond coupling to C4 was not resolved (<0.8 Hz).

1-Substituted 3,5-Dimethyladamantanes (3b and 3c). The ^{13}C chemical shifts and ^{13}C–^{13}C coupling constants of **3b** and **3c** are given in Table V. Assignments were based on SFORD experiments, ^{13}C–^{13}C coupling constants, and comparison to the results for **2a–f**.

2-Substituted Adamantanes (4a–c,g). The ^{13}C NMR data are compiled in Table VI. Most of the chemical shift assignments for the 2-substituted adamantanes have been reported in the literature, but there are several errors in the published assignments as noted in the table. This study of 2-methyladamantane-*11*-^{13}C shows that the assignments of Gerhards[42] are the correct ones. Assignments of C1 and C4[18] were shown to be incorrect in an SFORD experiment, and the assignments of C5 and C7 by Maciel et al.[43] and Barfield et al.[18] were shown to be reversed by means of the $^4J_{CC'}$; in **4a** the $^4J_{CC'}$ are 0.35 and 0.19 Hz and the calculated coupling constants are −0.34 and −0.16 Hz. This excellent agreement between experimental and calculated values as well as that for four-bond couplings in 1-substituted adamantanes is strong support for Gerhards' chemical shift assignments.

2-Substituted Bornanes (5, 6n,x, 7n,x, and 8). The ^{13}C chemical shifts and ^{13}C–^{13}C coupling constants in this series of compounds are compiled in Tables VII and VIII. Assignments were based on SFORD experiments, additivity relationships based on studies of related compounds,[9,44] and directly bonded and vicinal ^{13}C–^{13}C coupling constants. The methyl peaks of **6n**, **6x**, and the C10, C11, C5, and C6 carbons of **8** were identified by adding the shift reagent, tris(2,2,6,6-tetramethyl-3,5-heptanedionate)ytterbium, $Yb(dpm)_3$.

Carbons 10 and 11 in **7n** were assigned by the analogy of the 0.4-ppm chemical shift difference in **6n** and two compounds reported in ref 44. These indicate that an electronegative substituent in the 2-endo position deshields the *anti*-methyl C11. The ambiguous assignments involve the 10- and 11-methyl resonances in the exo isomer. Since neither C10 nor C11 had a measurable carbon–carbon coupling constant, no effort was made to complete the assignments.

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Registry No. 1a, 109-66-0; **1b**, 71-41-0; **1c**, 109-52-4; **2a**, 85553-56-6; **2b**, 65305-16-0; **2c**, 50530-21-7; **2e**, 85553-57-7; **3f**, 85553-58-8; **3b**, 85553-59-9; **3c**, 85553-60-2; **4a**, 56804-65-0; **4b**, 72490-93-8; **4c**, 50530-22-8; **4g**, 85553-61-3; **5**, 85553-62-4; **6n**, 85553-64-6; **6x**, 85553-63-5; **7n**, 85553-66-8; **7x**, 85553-65-7; **8**, 85553-67-9.

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