# Correlation of $^{13}$C−$^{1}$H Coupling Constants with Electronic Structure in Bi- and Polycycloalkanes: A PM3 and HF/6-31G* Analysis[†]

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Müller−Pritchard-type ($^{1}J_{^{13}\mathrm{C}-^{1}\mathrm{H}} = a \times \%\ \mathrm{s_C}$) and related expressions are explored for the prediction, from standard quantum chemical models, of one-bond C−H spin−spin coupling constants, in a series of bi- and polycyclics. Correlations of experimental $^{1}J_{^{13}\mathrm{C}-^{1}\mathrm{H}}$ with quantities computed from NBO analyses of PM3 and HF/6-31G* wave functions//geometries are critically examined for 38 aliphatic hydrocarbons (61 distinct tertiary C−H sites; $J$ range >100 Hz). Experimental vs calculated coupling constants are best fit when the model includes contributions from atomic charges ($q_\mathrm{H}$ and $q_\mathrm{C}$) along with s character at carbon (% $\mathrm{s_C}$). Previously used geometrical measures of hybridization are also discussed. The relationships obtained can be employed to easily predict one-bond C−H coupling constants at tertiary sites in polycyclic saturated hydrocarbons with experimentally useful accuracy. By using common computational chemistry methods for a large data set, we offer both a predictive tool for the practicing chemist and insights into the validity of hybridization-based interpretations of coupling.

## Introduction

Our interest in bicyclo[3.3.3]undecane (manxane) and its bridgehead radical[1] turned our attention to the use of one-bond C−H spin−spin coupling constants, $^{1}J_{^{13}\mathrm{C}-^{1}\mathrm{H}}$, as a physical property characteristic of hybridization effects on carbon.[2] Historically, experimental $^{1}J_{^{13}\mathrm{C}-^{1}\mathrm{H}}$ values have been interpreted in terms of the hybridization of the carbon orbitals in C−H bonds. Modern quantum chemical tools now allow easy access to self-consistent geometrical and structural data, even for fairly large molecules. This paper describes a search for a simple expression relating experimental tertiary $^{1}J_{^{13}\mathrm{C}-^{1}\mathrm{H}}$ values over a wide range of compounds to the hybridizations obtained from routine semiempirical and ab initio calculations. The results present both a broader test of the simple notion that hybridization determines C−H coupling, and a predictive tool that may help confirm structural assignments for unknown compounds.

The interpretation of the mechanism of spin−spin coupling is based on three types of electron-mediated interactions: (a) a Fermi contact interaction between the electron and nuclear spins, (b) a magnetic dipolar interaction between the electron and nuclear spins, and (c) an orbital interaction between the magnetic field produced by the orbital motion of the electrons and the nuclear magnetic dipole.[3] It is generally accepted that couplings involving hydrogen are dominated by the Fermi contact interaction,[4] a quantity that depends on the close approach of an electron to the nucleus and, accordingly, is a measure of the density of the bonding electrons at the nuclei. Since only s-orbitals have nonzero values at the nucleus and can therefore contribute to the contact interaction, the magnitude of the Fermi term is a measure of the s character of the bond at the two nuclei.

On the basis of the idea that the contact term is predominantly responsible for the C−H interactions, Müller and Pritchard[5] (MP) proposed a linear relationship (eq 1) between $^{1}J_{^{13}\mathrm{C}-^{1}\mathrm{H}}$ and the fraction of s character, $s_\mathrm{C}$, in the carbon hybrid orbital bonding to hydrogen. Hybridization arguments are based largely

$$^{1}J_{^{13}\mathrm{C}-^{1}\mathrm{H}} = 500 s_\mathrm{C} \quad (\mathrm{Hz}) \tag{1}$$

upon valence-bond (VB) or molecular orbital (MO) developments from Ramsey's second-order perturbation formula[3] for the Fermi contact term, using the average excitation energy ($\Delta E$) approximation, AEE.[6] Though such empirical assumptions have been criticized,[7] the procedure is justified by its success in describing qualitative features of spin−spin constants. Equation 2 shows one of the several equivalent forms that result from a SOS MO[8] treatment of the contact interaction in which the average $\Delta E$ is invoked.[9] In this expression $h$ is the Planck

$$^{1}J_{^{13}\mathrm{C}-^{1}\mathrm{H}} = (4/3)^2 h \mu_\mathrm{B}^2 \gamma_\mathrm{C} \gamma_\mathrm{H} (\Delta E)^{-1} s_\mathrm{C}^2(0)\, s_\mathrm{H}^2(0) P_{s_\mathrm{C}s_\mathrm{H}}^2 \tag{2}$$

constant, $\mu_\mathrm{B}$ is the Bohr magneton, $\gamma_\mathrm{C}$ and $\gamma_\mathrm{H}$ are the nuclear magnetogyric ratios, $s_\mathrm{C}^2(0)$ is the orbital density of a carbon 2s orbital at the C nucleus, $s_\mathrm{H}^2(0)$ is the orbital density of a hydrogen 1s orbital at the H nucleus, and $P_{s_\mathrm{C}s_\mathrm{H}}$ is the carbon 2s-hydrogen 1s element of the bond-order matrix. Interpretation of $^{1}J_{^{13}\mathrm{C}-^{1}\mathrm{H}}$ in terms of hybridization, or carbon s character, is based on the evaluation of the $P_{s_\mathrm{C}s_\mathrm{H}}^2$ term and effectively assumes $(\Delta E)^{-1} s_\mathrm{C}^2(0)\, s_\mathrm{H}^2(0)$ to be constant. If valence MOs are constructed from atomic orbitals $1\mathrm{s_H}$, $2\mathrm{s_C}$, and $2\mathrm{p_C}$, and overlap integrals are neglected, $P_{s_\mathrm{C}s_\mathrm{H}}$ is directly proportional to $a \cdot b$, where $a$ and $b$ represent atomic orbital coefficients for $1\mathrm{s_H}$ and $2\mathrm{s_C}$ in the C−H bonding MO, $\Psi_\mathrm{b}$ (eq 3). In addition,

$$\Psi_\mathrm{b} = a(1\mathrm{s_H}) + b(2\mathrm{s_C}) + c(2\mathrm{p_C}) \tag{3}$$

normalization of the MO (again, ignoring overlap) requires $a^2 + b^2 + c^2 = 1$, and sp$^n$ hybridization at carbon implies that $b^2 = c^2/n$. Using % $\mathrm{s_C}$ for the percent s character of the carbon atomic orbital in the C−H bond (% $\mathrm{s_C} = 100 s_\mathrm{C}$), it follows that

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[†] Dedicated to Professor G. J. Karabatsos on the occasion of his retirement celebration and 66th birthday.

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$$\%s_C = 100b^2/(b^2 + c^2) = 100b^2/(1 - a^2) = 100\,{}^1J_{^{13}C-^1H}/J_0a^2(1 - a^2) \qquad (4)$$

where $J_0$ is a constant to be determined empirically. The well-known MP relationship (eq 1) is derived from this equation for $a^2(1 - a^2) = 0.25$, the value for a pure covalent bond, and $J_0 = 2000$, as determined from the observed value of 125 Hz for $^1J_{^{13}C-^1H}$ in methane.[5]

The interpretation of this relation has been the subject of much controversy. Factors of possible importance in determining spin−spin coupling constants other than changes in hybridization—orbital electronegativities,[10] effective nuclear charge,[11] bond polarity,[12] and excitation energy[13]—have been extensively discussed in the literature; in hydrocarbons, where these quantities are not expected to vary sharply from molecule to molecule, the simple model of Müller and Pritchard is generally regarded as valid.

The MP relationship has been widely used in its original form or in modified versions to make quantitative predictions for nuclear spin couplings and to test theoretical models of molecular systems. Numerous linear correlations dealing with hybridization have been proposed in the literature.[14−19] Maksić et al.[19] introduced a modified relationship of the $^1J_{^{13}C-^1H}$ dependence on % $s_C$ with inclusion of C−H bond overlap, and Hu and Zhan[18] suggested an analogous relationship where bond overlap is replaced with bond order. Subsequently, starting from a theoretical analysis of the Fermi contact coupling interaction with inclusion of ionic terms to the C−H bond, Zhan and Hu[20] proposed a relationship for calculation of $^1J_{^{13}C-^1H}$ that includes contributions from both hybrid orbitals and net atomic charges. Nevertheless, the optimal form of the relationship between $^1J_{^{13}C-^1H}$ and hybridization at carbon depends upon the compounds investigated and the method of calculation.[21] Since one-bond C−H couplings serve as probes of steric strain and angle distortions, correlations of $^1J_{^{13}C-^1H}$ have also been explored with internuclear[22] or interorbital CCC bond angles,[23] the sum of internuclear CCC bond angle distortions,[24] or strain energy.[25]

The need to restrict the correlations to a given fragment type and to be consistent with regard to geometries for the compounds under study led us to reevaluate the MP-type relationships for strained aliphatic hydrocarbons, where previous methods gave less satisfactory results. With the ready availability of wave functions for geometry optimized structures from which hybridization information can be directly drawn, it seems appropriate to seek a correlation by which C−H couplings can be predicted from easily obtained computational results for compounds of nontrivial size.

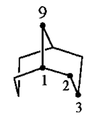
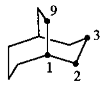
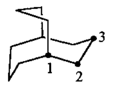
## Theoretical Model

Optimized geometries of compounds **1**−**38** were obtained by using the semiempirical PM3[26] and the ab initio HF/6-31G*[27] methods.[28] Hybridizations of carbon atoms and atomic charges in **1**−**38** were computed from PM3 and HF/6-31G* optimized geometries using the natural bond orbital (NBO) analysis[29] as implemented in the SPARTAN package.

## Results and Discussion

The $^{13}C$ NMR chemical shifts and one-bond C−H coupling constants measured experimentally in this work for bicyclo[3.3.l]nonane **35**, bicyclo[3.3.2]decane **36**, and bicyclo[3.3.3]undecane **38** are presented in Table 1. The series of compounds considered here, **1**−**38**, includes all similar compounds referenced in previous studies and is substantially augmented with other polycyclic saturated hydrocarbons that provide experimental $^1J_{^{13}C-^1H}$ values ranging from 120 Hz to 215 Hz. Table 2 lists the experimental $^1J_{^{13}C-^1H}$ couplings for **1**−**38**, together with the percent s character, % $s_C$, in the C−H bonding hybrids. Selected PM3 and HF/6-31G* geometrical parameters and natural atomic charges for the bridgehead sites in **1**−**38** are included in the Supporting Information (Tables 1S and 2S).

**TABLE 1: $^{13}C$ NMR Chemical Shifts and Experimental $^1J_{^{13}C-^1H}$ Coupling Constants**

| Compound | Carbon | δ (ppm) | $^1J_{^{13}C-^1H}$ (Hz) |
|---|---|---|---|
| Bicyclo[3.3.1]nonane **35**[a] | | | |
|  | 1 | 27.9 | 129.4 |
| | 2 | 31.6 | 127.4 |
| | 3 | 22.5 | 125.6 |
| | 9 | 35.0 | 128.3 |
| Bicyclo[3.3.2]decane **36**[b] | | | |
|  | 1 | 33.7 | 125.2 |
| | 2 | 32.9 | 123.4 |
| | 3 | 22.8 | 124.3 |
| | 9 | 30.4 | 125.3 |
| Bicyclo[3.3.3]undecane **38**[c] | | | |
|  | 1 | 30.7 | 120.0 |
| | 2 | 28.9 | 124.2 |
| | 3 | 20.1 | 125.0 |

[a] The $^{13}C$ NMR spectrum of **35** is in agreement with previous literature reports. See: Heumann, A.; Kolshorn, H. *Tetrahedron* **1975**, *31*, 1571. [b] The $^{13}C$ NMR signals of **36** are attributed to the corresponding carbons based on proton assignments and H/C correlations from the 2D HMQC spectrum of **36**. [c] The individual assignments of the $^{13}C$ peaks of **38** are based on the relative intensities of the signals and their multiplicity in the off-resonance proton-decoupled spectrum of **38**.

The computed natural hybrids, shown in Table 2, agree with known trends such as those summarized in Bent's rule,[30] where atomic s character concentrates in orbitals directed toward electropositive substituents. Successive shortening of the bridges is reflected in more polarized C−H bonds[31] and, thus, increased s character in the C−H bonding MO. Also, enhanced C−H bond p character, accompanied by wide CCC angles, is associated with reduced experimental $^1J_{^{13}C-^1H}$ couplings. The changes in the PM3 geometries of **1**−**38** vs the corresponding ab initio HF/6-31G* geometries are significant only regarding the C−H bond lengths, which are shorter at the ab initio level[32] and correlate surprisingly poorly with the semiempirical values (the correlation coefficient, *R*, for a linear fit of PM3 vs HF/6-31G* C−H bond lengths is 0.8). Regardless of bond length differences, the PM3 and HF/6-31G* hybridizations at carbon in the C−H bonding orbitals correlate extremely well ($R = 0.996$ and s.d. = 0.37 for the linear fit of % $s_{C,PM3}$ vs % $s_{C,HF/6-31G}$); even though they differ numerically, they are similar if qualitative features are concerned. As orbital hybridization can be related to many molecular properties of interest, it is desirable to know the "best hybrids" for a given molecule. Comparison of the PM3 and HF/6-31G* hybrids with the empirical ones obtained from eq 1 and experimental $^1J_{^{13}C-^1H}$ couplings reveals that while the PM3 hybrids are systematically higher then the empirical standard couplings predicted by eq 1, the ab initio values are consistently below it. To our surprise, the % $s_C$ in the idealized canonical cases: sp ($C_2H_2$), sp$^2$ ($C_2H_4$), and sp$^3$ ($CH_4$), is better reproduced when the natural hybrids derive from the PM3 wave function (% $s_C$: 51.1, 33.2, and 25.0) than from

**TABLE 2: Experimental One-Bond C−H Spin−Spin Coupling Constants ${}^1J_{^{13}C-^{1}H}$ (in Hz) and Calculated % $s_C$ Character of the Carbon Hybrid Forming the C−H Bonds in 1−38**

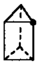
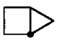
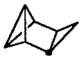
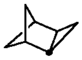
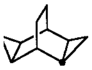
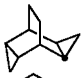
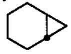
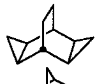
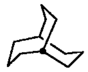
| No.[a] | Compound | ${}^1J_{^{13}C-^{1}H}$ [b] | % $s_C$ PM3 | % $s_C$ HF/6-31G* | Symmetry[c] |
|---|---|---|---|---|---|
| **1a** |  | 215[d] | 41.2 | 34.9 | $C_s$ |
| **2a** |  | 212[e] | 41.2 | 34.9 | $C_{2v}$ |
| **3** |  | 210[f] | 42.5 | 36.4 | $C_{2v}$ |
| **1b** |  | 209[d] | 41.1 | 34.9 | $C_s$ |
| **4** |  | 205[g] | 40.4 | 33.8 | $C_{2v}$ |
| **5a*** |  | 200.3[h] | 40.45 | 33.65 | $C_s$ |
| **6a** |  | 190[i] | 39.7 | 32.5 | $C_2$ |
| **7a** |  | 189[j] | 39.9 | 33.9 | $C_s$ |
| **8a** |  | 185[k] | 38.1 | 32.2 | $C_{2v}$ |
| **9** |  | 179.7[l] | 39.4 | 33.6 | $D_{3h}$ |
| **10** |  | 179[k] | 37.2 | 30.7 | $C_{2h}$ |
| **11** |  | 178.1[k] | 37.0 | 31.0 | $C_s$ |
| **7b** |  | 177.2[j] | 37.7 | 31.6 | $C_s$ |
| **12a** |  | 175[m] | 36.3 | 30.3 | $C_{3v}$ |
| **13a** |  | 174[n] | 36.1 | 30.3 | $C_{2v}$ |
| **14a** |  | 171[o] | 36.1 | 30.1 | $C_{2v}$ |
| **1c** |  | 171[d] | 35.5 | 29.3 | $C_s$ |
| **13b** |  | 171[n] | 35.9 | 29.8 | $C_{2v}$ |
| **15a** |  | 169[p] | 35.5 | 29.2 | $C_s$ |
| **16** |  | 167.8[q] | 36.8 | 30.3 | $D_{3h}$ |
| **14b** |  | 166[o] | 35.3 | 29.2 | $C_{2v}$ |
| **8b** |  | 166[k] | 35.7 | 29.6 | $C_{2v}$ |
| **17a** |  | 166[o] | 33.8 | 27.6 | $C_s$ |
| **1d** |  | 166[d] | 36.6 | 30.4 | $C_s$ |
| **18*** |  | 165.7[r] | 34.6 | 28.7 | $C_s$ |
| **19a** |  | 165[o] | 33.9 | 27.6 | $C_s$ |
| **20a** |  | 164[o] | 33.8 | 27.6 | $C_{2v}$ |
| **2b** |  | 163[e] | 36.4 | 30.3 | $C_{2v}$ |
| **17b** |  | 161[o] | 33.8 | 27.7 | $C_s$ |
| **21*** |  | 160[d] | 32.9 | 26.95 | $C_1$ |
| **7c** |  | 158.8[j] | 35.9 | 29.8 | $C_s$ |
| **22a** |  | 157.9[s] | 36.7 | 30.7 | $C_{3v}$ |
| **23a** |  | 157[n] | 36.5 | 30.8 | $C_{2v}$ |
| **24** |  | 154.5[t] | 36.5 | 30.8 | $O_h$ |
| **5b** |  | 154.2[h] | 34.0 | 28.2 | $C_s$ |
| **15b** |  | 152[p] | 34.6 | 28.5 | $C_s$ |
| **23b** |  | 152[n] | 35.2 | 29.3 | $C_{2v}$ |
| **25** |  | 151.8[p] | 34.5 | 28.5 | $C_{2v}$ |
| **22b** |  | 148.8[s] | 34.1 | 28.3 | $C_{3v}$ |
| **12b** |  | 148[m] | 33.0 | 27.3 | $C_{3v}$ |
| **26** |  | 148[u] | 34.5 | 28.8 | $D_{5h}$ |
| **27** |  | 147.9[s] | 32.5 | 27.8 | $D_{2d}$ |
| **23c** |  | 146[n] | 33.4 | 27.5 | $C_{2v}$ |
| **6b** |  | 145[i] | 31.9 | 26.4 | $C_2$ |
| **28** |  | 144.9[s] | 32.3 | 26.5 | $C_s$ |
| **13c** |  | 144[n] | 32.7 | 26.9 | $C_{2v}$ |
| **29** |  | 141.0[v] | 31.8 | 26.3 | $C_{2v}$ |
| **30** |  | 137.0[w] | 30.1 | 24.5 | $C_{3h}$ |
| **14c** |  | 137[o] | 30.2 | 24.5 | $C_{2v}$ |
| **17c** |  | 136.2[o] | 29.8 | 24.3 | $C_s$ |
| **31*** |  | 136[i] | 31.0 | 25 | $C_2$ |
| **32** |  | 134.5[o] | 29.1 | 24.0 | $D_{3h}$ |
| **19b** |  | 134[o] | 29.5 | 24.2 | $C_s$ |
| **33*** |  | 133.7[x] | 29.9 | 24.5 | $C_s$ |
| **34** |  | 133.4[v] | 29.2 | 23.8 | $T_d$ |

**TABLE 2 (Continued)**

| No.[a] | Compound | ${}^1J_{^{13}C-^1H}$ [b] | % $s_C$ PM3 | % $s_C$ HF/6-31G* | Symmetry[c] | No.[a] | Compound | ${}^1J_{^{13}C-^1H}$ [b] | % $s_C$ PM3 | % $s_C$ HF/6-31G* | Symmetry[c] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **20b** |  | 133[o] | 29.8 | 24.2 | $C_{2v}$ | **37a*** |  | 122.4[z] | 25.7 | 21.9 | $C_3$ |
| **35*** |  | 129.4[y] | 28.1 | 22.8 | $C_{2v}$ | **38*** |  | 120.0[y] | 26.5 | 21.0 | $C_{3h}$ |
| **36*** |  | 125.2[y] | 26.8 | 21.5 | $C_s$ | **37b*** |  | 111.2[z] | 25.2 | 20.1 | $C_3$ |

[a] Asterisk (*) denotes an energy-weighted average over conformations. [b] For several compounds considered here, various literature reports present different values for the one-bond C−H coupling constants; in such cases the most recent literature reference was considered. [c] Symmetry of lowest energy geometry. [d] Christl, M. *Chem. Ber.* **1975**, *108,* 2781. [e] Christl, M.; Brüntrup, G. *Chem. Ber.* **1974**, *107,* 3908. [f] Andrews, G. D.; Baldwin, J. E. *J. Am. Chem. Soc.* **1977**, *99,* 4851. [g] Withrich, K.; Meiboom, S.; Snyder, L. C. *J. Chem. Phys.* **1970**, *52,* 230. [h] Della, E. W.; Hine, P. T.; Patney, H. K. *J. Org Chem.* **1977**, *42,* 17. [i] Christl, M.; Herzog, C. *Chem. Ber.* **1986**, *119,* 3067. [j] Christl, M.; Leininger, H.; Mattauch, B. *Spectrosc. Int. J.* **1983**, *2,* 184. [k] Figeys, H. P.; Geerlings, P.; Raeymaekers, P.; Van Lommen, G.; Defay, N. *Tetrahedron* **1975**, *31,* 1731. [l] Katz, T. J.; Acton, N. *J. Am. Chem. Soc.* **1973**, *95,* 2738. [m] Olah, G. A.; White, A. M. *J. Am. Chem. Soc.* **1969**, *91,* 3954. [n] Hamlin, J. E.; Toyne, K. J. *J. Chem. Soc., Perkin Trans 1* **1981**, 2731. [o] Gunther, H.; Herrig, W.; Seel, H.; Tobias, S. *J. Org. Chem.* **1980**, *45,* 4329. [p] Christl, M.; Herbert, R *Org. Magn. Reson.* **1979**, *12,* 150. [q] Lazzaretti, P.; Malagoli, M.; Zanasi, R.; Della, E. W.; Lochert, I. J.; Giribet, C. G.; Ruiz de Azna, M. C.; Contreras, R H. *J. Chem. Soc., Faraday Trans.* **1995**, *91,* 4031. [r] Shustov, G. V.; Denisenko, S. N.; Chervin, I. I.; Asfandiarov, N. L.; Kostyanovsky, R G. *Tetrahedron* **1985**, *41,* 5719. [s] Della, E. W.; Cotsaris, E.; Hine, P. T.; Pigou, P. E. *Aust. J. Chem.* **1981**, *34,* 913. [t] Axenrod, T.; Liang, B.; Bashir-Hasheuri, A.; Dave, P. R.; Reddy, D. S. *Magn. Reson. Chem.* **1991**, *29,* 88. [u] Eaton, P. E.; Or, Y. S.; Branca, S. J. *J. Am. Chem. Soc.* **1981**, *103,* 2134. [v] Schneider, H. J.; Heiske, D.; Hoppen, W.; Thomas, F. *Tetrahedron* **1977**, *33,* 1769. [w] de Meijere, A.; Schallner, O.; Weitemeyer, C.; Spielmann, W. *Chem. Ber.* **1979**, *112,* 908. [x] Kovaček, D.; Maksić, Z. B.; Elbel, S.; Kudnig, J. *J. Mol. Struct.* **1994**, *304,* 247. [y] This work. [z] McMurry, J. E.; Lectka, T.; Hodge, C. N. *J. Am. Chem. Soc.* **1989**, *111,* 8867.

**TABLE 3: Previously Reported Semiempirical Correlations of Experimental ${}^1J_{^{13}C-^1H}$ Coupling Constants with Hybridization, Bond Angles, or Atomic Charges in Hydrocarbons**

| relationship | | s.d.[a] | no. data[b] | ref |
|---|---|---|---|---|
| ${}^1J_{^{13}C-^1H} = 5.00(\%\ s_C)$ | (1) | | | 5a |
| ${}^1J_{^{13}C-^1H} = 5.70(\%\ s_C) - 18.4$ | (5) | 5.7 | 19 | 19 |
| ${}^1J_{^{13}C-^1H} = 6.93(\%\ s_C) - 51.06$ | (6) | 5.0 | 11 | 15a |
| ${}^1J_{^{13}C-^1H} = 6.91(\%\ s_C) - 72.39$ | (7) | 5.0 | 17 | 15b |
| ${}^1J_{^{13}C-^1H} = 6.16(\%\ s_C) - 23.95$ | (8) | 3.6 | 14 | 18 |
| ${}^1J_{^{13}C-^1H} = 3.16(\%\ s_C) + 49.9$ | (9) | 1.7 | 7 | 16 |
| ${}^1J_{^{13}C-^1H} = 0.769(\%\ s_C)^{3/2} + 6.5$ | (10) | 5.9 | 17 | 17 |
| ${}^1J_{^{13}C-^1H} = -0.72\theta_{CCC}^{av} + 203$ | (11) | 2.4 | 10 | 22a |
| ${}^1J_{^{13}C-^1H} = (6.12 \times 10^{-5})(\Sigma\Delta\theta_{CCC})^2 + 0.65\Sigma\Delta\theta_{CCC} + 131.26$ | (12) | 4.2[c] | 30 | 24a |
| ${}^1J_{^{13}C-^1H} = 10.79(\%\ s_C)/(1 + S_{C-H}^2) - 54.9$ | (13)[d] | 5.2 | 37 | 19 |
| ${}^1J_{^{13}C-^1H} = 17.063(\%\ s_C)/[(4/3)^2 + P_{C-H}^2] - 25.0$ | (14)[e] | 3.4 | 14 | 18 |
| ${}^1J_{^{13}C-^1H} = 0.42\mathrm{SE} + 124.8$ | (15)[f] | 0.3 | 4 | 25 |
| ${}^1J_{^{13}C-^1H} = (-8.81 \times 10^3)q_H q_C + 114.74$ | (16)[g] | 3.8 | 21 | 36 |
| ${}^1J_{^{13}C-^1H} = (6.118 + 0.903q_C)(\%\ s_C) + 94.42q_H - 22.27$ | (17) | 4.5 | 14 | 20 |

[a] Standard deviation (in Hz) of experimental vs calculated one-bond C−H spin−spin coupling constants from literature data (the literature reported numbers for standard deviation are given here with two significant figures). [b] Number of independent ${}^1J_{C-H}$ values used in the correlation. [c] The literature reported standard deviation of 2.74 Hz is in error. [d] $S_{C-H}$ is the overlap integral. [e] $P_{C-H}$ is C−H bond order. [f] SE is strain energy. [g] $q_H$ and $q_C$ are atomic charges.

the HF/6-31G* one (% $s_C$: 47.7, 30.1, and 25.0); however, none of the PM3 % $s_C$ values in Table 2 is <25 even for **37**−**38**. While each method needs its own correlation, it would be of interest to compare the semiempirical and ab initio natural hybrids for a number of systems, in order to estimate the relative effects of various approximations at the particular levels of theory considered.

In previous studies of empirical relationships between ${}^1J_{^{13}C-^1H}$ and hybridization or bond angles, summarized in Table 3, the choice of compounds was arbitrary and those with large deviations of calculated vs experimental ${}^1J_{^{13}C-^1H}$ couplings, such as strained polycyclics, were generally excluded, obviating meaningful comparisons between different correlations. Most studies used both experimental and calculated geometries (employing INDO,[14−15,17,19] AM1,[16] CNDO/2,[18,20] or MM[24a,25] methods), which could be a source of systematic deviations, too, while conformational averaging was ignored in most cases. Hybridization parameters were extracted with different methods; most gave the same general picture,[21] but some give unsatisfactory results for highly strained cyclopropane ring compounds. Some of the correlations[16,25] are based on too few compounds to be of general use. Furthermore, in light of Gil's[17] finding that residual delocalization makes Δ*E* dependent on carbon coordination number, it is arguably inappropriate to directly include primary, secondary, and tertiary C−H sites in the same correlation, which all previous studies have done. Instead, we have focused this initial effort on prediction of tertiary C−H coupling constants for the widest possible range of hydrocarbons.

The basic MP-type relationships are reexamined for the hydrocarbons listed in Table 2. The PM3 correlations established by least-squares analysis[33] are presented in Table 4. In comparison with the original MP relationships[5] (eq 1) we found, as have others before us, that better concordance between experimental and calculated ${}^1J_{^{13}C-^1H}$ values is obtained when a constant term, usually negative, is added to eq 1, (compare eqs 18 and 19, Table 4). This constant term is generally considered to originate in the deficiencies of the AEE approach and the assumption of Fermi contact term predominance.[34] Maksić et al.[19] suggest that the constant term results from the ionic character of C−H bonds, a point examined (and discarded) by Müller and Pritchard[5] themselves. Since the semiempirical PM3 method may introduce errors, we have also used the ab initio HF/6-31G* model to see whether the agreement between ${}^1J_{^{13}C-^1H}$ and % $s_C$ can be refined by a higher level calculation. No improvement was found in the correlation of ${}^1J_{^{13}C-^1H}$ with percent s character determined from the HF/6-31G* wave functions of **1**−**38** (Figure 1), which suggests that the deviations from linearity seen in subsequent correlations are not an artifact of the PM3 method. The difference between experimental and calculated ${}^1J_{^{13}C-^1H}$ is especially high when the carbon atom at the tertiary site is contained in at least two three- or four-

**TABLE 4: Semiempirical Relationships between Experimental $^{1}J_{^{13}C-^{1}H}$ and Hybridization, C−H Distance, C−H Bond Order, Natural Atomic Charges on Carbon and Hydrogen, or Internuclear Angles, Established by Least-Squares Analysis for the PM3 Optimized Geometries of Hydrocarbons 1−38[a]**

| semiempirical relationships | | s.d.[b] |
|---|---|---|
| $^{1}J_{^{13}C-^{1}H} = 4.66(\%\ s_C)$ | (18) | 8.4 |
| $^{1}J_{^{13}C-^{1}H} = 5.61(\%\ s_C) - 33.04$ | (19) | 7.5 |
| $^{1}J_{^{13}C-^{1}H} = 0.65(\%\ s_C)^{3/2} + 28.90$ | (20) | 7.1 |
| $^{1}J_{^{13}C-^{1}H} = 0.20(\%\ s_C)/(-1.58 + 3.01d_{C-H} - 1.41d^{2}_{C-H}) - 171.67$ | (21)[c] | 6.2 |
| $^{1}J_{^{13}C-^{1}H} = 0.83(\%\ s_C)/(-0.71 + P^{2}_{C-H}) + 28.72$ | (22)[d] | 6.3 |
| $^{1}J_{^{13}C-^{1}H} = -2655.22q_{H}q_{C} + 128.80$ | (23) | 10.6 |
| $^{1}J_{^{13}C-^{1}H} = 3.78(\%\ s_C) + 1151.42\lvert q_{H}q_{C}\rvert + 16.28$ | (24)[e] | 5.2 |
| $^{1}J_{^{13}C-^{1}H} = 3.23(\%\ s_C) - 2.83(\%\ s_C)q_C + 193.84q_H + 18.90$ | (25) | 5.4 |
| $^{1}J_{^{13}C-^{1}H} = 3.77(\%\ s_C) - 2229.80q_{H}q_{C} + 137.43q_C - 76.72q_H + 26.45$ | (26) | 4.8 |
| $^{1}J_{^{13}C-^{1}H} = -1.95\theta^{av}_{CCC} + 344.69$ | (27) | 6.4 |
| $^{1}J_{^{13}C-^{1}H} = 131.23 + 0.66\Sigma\Delta\theta_{CCC} - (6.56 \times 10^{-5})(\Sigma\Delta\theta_{CCC})^{2}$ | (28) | 6.3 |
| $^{1}J_{^{13}C-^{1}H} = 902.82q_H + 73.15$ | (29)[f] | 4.6 |
| $^{1}J_{^{13}C-^{1}H} = -2289.32a_{1s_H} + 1697.49$ | (30) | 4.7 |

[a] Correlations 18−30 include all 61 independent data points from Table 2. [b] One-bond C−H coupling constants and standard deviations (s.d.) are given in Hz. [c] $d_{C-H}$ is C−H bond distance in Å. On the basis of eq 13 (Table 3) and the reported near-linear dependence of $S_{C-H}$ on $d_{C-H}$ (ref 35), the denominator in eq 21 was approximated as a second-order polynomial in $d_{C-H}$; all five numerical values represent free parameters. [d] $P_{C-H}$ is Mulliken C−H bond order. [e] This relation, kindly suggested by an anonymous reviewer, keeps the number of terms in the regression low while including hybridization and bond ionicity economically. [f] Equations 29−30 use only 60 independent data points; **37a** is excluded from these correlations.

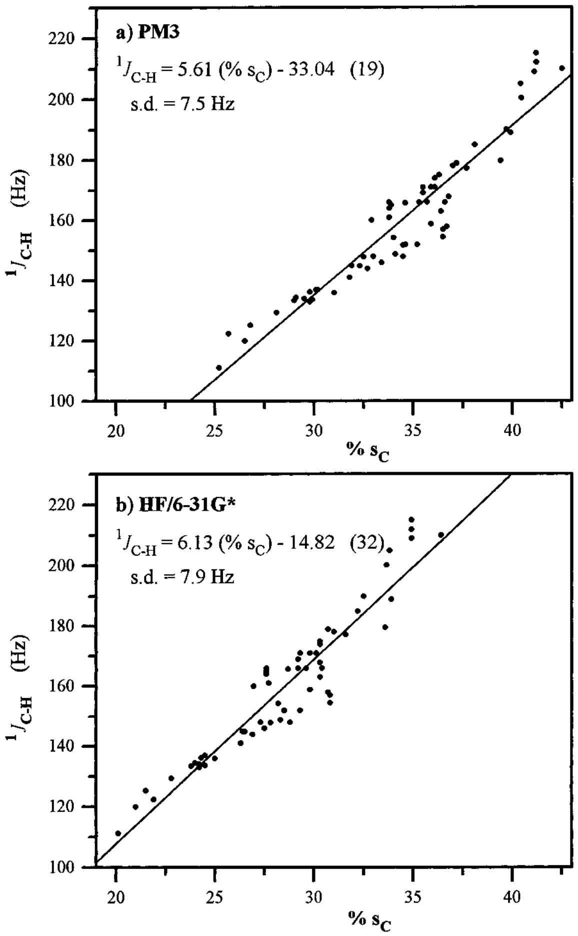


**Figure 1.** Experimental one-bond C−H spin−spin coupling constants, $^{1}J_{^{13}C-^{1}H}$ vs percent s character, % $s_C$, of the C hybrid in the C−H bonding orbital obtained from NBO analysis of (a) PM3 and (b) HF/6-31G* wave functions for optimized geometries of **1**−**38**.

membered rings. It is probable that these deviations occur as a result of breakdown of the AEE approximation in strained rings.

The relationship proposed by Gil[17] and based on the variation of Δ*E* with carbon coordination number was also investigated (eq 20, Table 4). In the present case, however, there is no physical justification for the improved fit over eq 19.

The Spartan software does not explicitly report overlap integrals, so we examined the basic relationship of Maksić et al.[19] (eq 13, Table 3) for **1**−**38** by replacing bond overlap with either C−H distance (overlap is a nearly linear function of distance in the range of interest)[35] or C−H bond order (NBO-derived), as proposed by Zhan and Hu[21b] (eq 14, Table 3). The relations obtained (eqs 21−22, Table 4) do not show significant improvement over the simple linear dependence of $^{1}J_{^{13}C-^{1}H}$ on % $s_C$. A possible semiempirical relationship of $^{1}J_{^{13}C-^{1}H}$ with C−H bond order was also explored, but no improvement over those involving only hybridization and atomic charges was obtained.

The best correlations are obtained by including the atomic charges $q_C$ and $q_H$ calculated by natural population analysis for C and H (eqs 24−26, Table 4). Previously, Guillen and Gasteiger[36] used the iterative partial equalization of orbital electronegativity method (PEOE) for calculating atomic partial charges in hydrocarbons with three- and four-membered rings and established a linear correlation between $^{1}J_{^{13}C-^{1}H}$ and the product of C and H charges (eq 16, Table 3). The PEOE procedure reproduces surprisingly well small trends in the coupling constants, even though hybridization states, calculated from substitution patterns, are taken to be artificially equal for distinct compounds, as, for example, **4** and **5a**. Zhan and Hu[20] introduced a generalized relationship suitable for both hydrocarbons and molecules with I$^+$ and I$^-$ substituents, where $^{1}J_{^{13}C-^{1}H}$ is calculated from the s character of the hybrids and the net atomic charges on C and H (eq 16, Table 3). This semiempirical expression is derived from the usual second-order perturbation formula for the Fermi contact term,[3] where ionic contributions are included in the C−H bonding MO and considered to be related with the net charges on C and H. Such a correlation applied to **1**−**38** (eq 25, Table 4) gives a much lower s.d. as compared to eqs 18−22, which indicates that while hybridization is important in the study of one-bond C−H spin−spin coupling constants, the ionic contribution to bridgehead C−H bonds cannot be neglected. Similarly, in their VB treatment of the Fermi contact interaction between directly bonded atoms, Karplus, Grant, and Lichtman[11b,37] concluded that $^{1}J_{^{13}C-^{1}H}$ not only depends on hybridization but also is directly proportional with the effective nuclear charge, implying that the C−H bond ionicity may not be ignored. Various forms of semiempirical relationship correlating $^{1}J_{^{13}C-^{1}H}$ vs hybridization, $q_H$, and $q_C$ have been tested, among which eq 26, with the most free parameters, gave as expected the lowest standard deviation (see Figure 2).[38] Correlation of $^{1}J_{^{13}C-^{1}H}$ solely with the product of charges $q_{H}q_{C}$, (eq 23, Table 4), gives a poorer fit.

Interestingly, the best single-parameter correlations are the PM3 $q_H$ or the PM3 atomic orbital coefficient on H, $a_{1s_H}$ (or *a*, see eq 3), and experimental $^{1}J_{^{13}C-^{1}H}$ (eqs 29−30, Table 4).[39] If **37a** (the *in*-C−H bond of bicyclo[4.4.4]tetradecane) is excluded

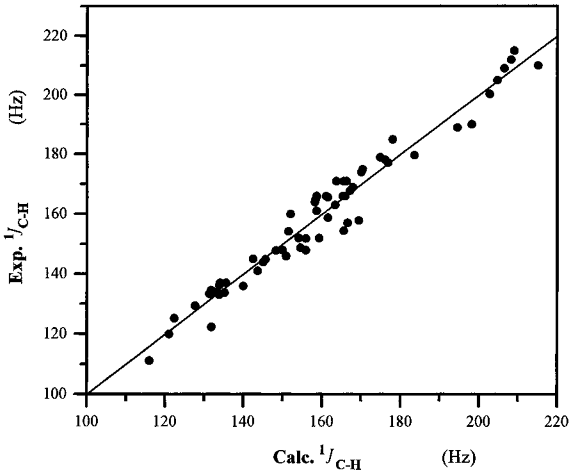


**Figure 2.** Plot of experimental vs calculated (eq 26) one-bond C−H spin−spin coupling constants, $^1J_{^{13}C-^1H}$, in **1**−**38**.

from the correlations,[40] linear relationships are obtained via least-squares analysis with standard deviations of only 4.7 Hz (Figure 3).

The relationship between one-bond C−H spin−spin coupling constants and calculated bond angles has also been investigated (eqs 27−28, Table 4). Average CCC angles, $\theta^{av}_{CCC} = (\sum\angle CCC°)/3$, were considered for the general case of three substituents attached to a methine carbon; again, conformational averaging was included where necessary. The PM3 empirical relationships established via least-squares analysis are recorded in Table 4. As expected, similar standard deviations are found for plots of $^1J_{^{13}C-^1H}$ vs the average CCC angles, $\theta^{av}_{CCC}$, or the sum of internuclear angle distortions, $\sum\Delta\theta_{CCC} = \sum\,(109.5° - \angle CCC°)$.

It is recognized that bent bonds[41] are frequently found in organic compounds and internuclear bonds do not always correspond to bond paths,[42] defined as the path of maximum charge density between the bonded atoms. Hybridization is more closely related to interorbital rather than internuclear angles. A simple analysis of the correlation of $^1J_{^{13}C-^1H}$ with bond path angles vs internuclear angles in methine systems with $C_{3v}$ symmetry supports this idea and allows for a qualitative estimate of the amount of bond bending. Thus, we converted the corresponding hybridization, sp$^n$, at carbons with local $C_{3v}$ symmetry into interorbital angles, $\theta^{\circ}_{CCC}$, using Coulson's relation:[43]

$$\theta^{\circ}_{CCC} = \arccos\left(-\frac{1}{n}\right) \tag{9}$$

**TABLE 5: Semiempirical Relationships between Experimental $^1J_{^{13}C-^1H}$ and Hybridization, Natural Atomic Charges on Carbon and Hydrogen, or Internuclear Angles, Established by Least-Squares Analysis for the HF/6-31G* Optimized Geometries of Hydrocarbons 1−38[a]**

| semiempirical relationships | | s.d.[b] |
|---|---|---|
| $^1J_{^{13}C-^1H} = 5.62(\%\ s_C)$ | (31) | 8.0 |
| $^1J_{^{13}C-^1H} = 6.13(\%\ s_C) - 14.82$ | (32) | 7.9 |
| $^1J_{^{13}C-^1H} = 0.77(\%\ s_C)^{3/2} + 41.50$ | (33) | 7.5 |
| $^1J_{^{13}C-^1H} = 1.50(\%\ s_C) - 19.30(\%\ s_C)q_C - 137.10q_H + 17.17$ | (34) | 5.5 |
| $^1J_{^{13}C-^1H} = 6.21(\%\ s_C) - 1397.98q_Hq_C - 263.37q_C - 496.20q_H - 42.79$ | (35) | 5.6 |
| $^1J_{^{13}C-^1H} = -1.91\theta^{av}_{CCC} + 341.72$ | (36) | 6.4 |
| $^1J_{^{13}C-^1H} = 132.04 + 0.65\sum\Delta\theta_{CCC} - (1.53 \times 10^{-4})(\sum\Delta\theta_{CCC})^2$ | (37) | 6.5 |

[a] Correlations 30−37 include all 61 independent data points from Table 2. [b] One-bond C−H coupling constants and standard deviations (s.d.) are given in Hz.

The results show improved correlation of $^1J_{^{13}C-^1H}$ with $\theta^{\circ}_{CCC}$ (s.d. is 4.4 Hz for PM3 geometries and 4.2 Hz for HF/6-31G* geometries) as compared with $\theta_{CCC}$ (s.d. is 5.1 Hz for PM3 geometries and 4.8 Hz for HF/6-31G* geometries).[44] It seems worthwhile in future work to examine the correlation of $^1J_{^{13}C-^1H}$ with an average CCC bond path angle defined in terms of charge density.[45]

A similar analysis was performed for the HF/6-31G* optimized geometries of **1**−**38**. The relationships obtained are presented in Table 5 and, analogously with the PM3 results, show that inclusion of C and H atomic charges improve considerably the simple correlation of $^1J_{^{13}C-^1H}$ with hybridization. Nevertheless, the 6-31G* results are less correlated with experiment than those from the PM3 method, in accord with the conclusion of Edison et al.[7b] that better agreement with experimental values is obtained for calculated nuclear spin−spin coupling constants when using modest levels of MO theory. More disturbing are the HF/6-31G* natural atomic charges on hydrogen and carbon in **1**−**38**, whose oscillating behavior and poor correlation with PM3 charges is surprising. The striking discrepancy at the PM3 level of the H and C atomic charges in **37a** vs other bridgehead sites with similar hybridization at carbon, however, is reduced at the HF/6-31G* level of calculation.

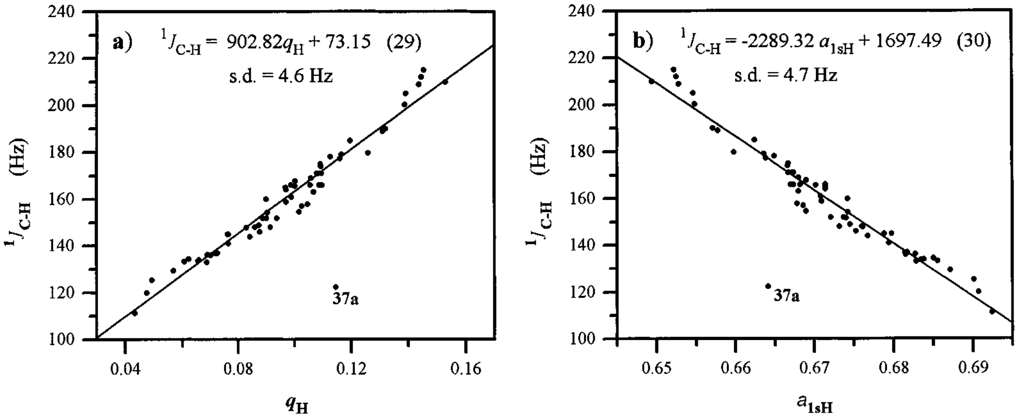


**Figure 3.** Experimental one-bond C−H spin−spin coupling constants, $^1J_{^{13}C-^1H}$, in **1**−**38** vs (a) PM3 natural atomic charge on hydrogen, $q_H$ (eq 29), and (b) PM3 atomic orbital coefficient on hydrogen, $a_{1s_H}$ (eq 30). Note: **37a** is excluded from the correlations.

## Summary

(1) The experimental values of $^{13}C$ NMR chemical shifts and one-bond C−H coupling constants in bicyclo[3.3.1]nonane **35**, bicyclo[3.3.2]decane **36**, and bicyclo[3.3.3]undecane **38** are reported. (2) Semiempirical relationships of experimental $^{1}J_{^{13}\mathrm{C}-^{1}\mathrm{H}}$ with % $s_C$, $q_H$ and $q_C$, $a_{1s_H}$, $\theta^{av}_{CCC}$, and $\sum\Delta\theta_{CCC}$, are examined for compounds **1**−**38** and show reasonable agreement of calculated vs experimental $^{1}J_{^{13}\mathrm{C}-^{1}\mathrm{H}}$ values (Tables 4 and 5). The PM3 model shows particular promise; the computations required for geometry optimization and NBO analysis are modest and can be carried out with readily available electronic structure packages. Correlation of experimental $^{1}J_{^{13}\mathrm{C}-^{1}\mathrm{H}}$ with PM3 hybridization is considerably improved by inclusion of natural atomic charges on carbon and hydrogen (eqs 24−26) to give best fits of experimental vs calculated $^{1}J_{^{13}\mathrm{C}-^{1}\mathrm{H}}$ coupling constants (s.d. = 4.8 Hz for eq 26; 61 data points). Such an empirical relation is useful for predicting $^{1}J_{^{13}\mathrm{C}-^{1}\mathrm{H}}$ for hypothetical compounds by comparison with experiment, but offers little physical insight into the coupling mechanisms. However, surprisingly good single-parameter linear correlations of $^{1}J_{^{13}\mathrm{C}-^{1}\mathrm{H}}$ with PM3 $q_H$ (eq 29; 60 data points, s.d. = 4.6 Hz) or $a_{1s_H}$ (eq 30; 60 data points, s.d. = 4.7 Hz) are found for **1**−**38**, when the distant outlier **37a** is removed. (3) That $^{1}J_{^{13}\mathrm{C}-^{1}\mathrm{H}}$ depends on carbon orbital hybridization is part of the canon of organic chemistry. Numerous equations have been previously proposed based on modest data sets and various measures of hybridization. However, in most cases the choice of compounds was arbitrary and their geometries were inconsistent, while the correlations established gave less satisfactory results for strained polycyclics. On the basis of the comparison between various MP-type relationships and the critical evaluation of their performance for our wide range of compounds, we conclude that ionic contributions to C−H bonds are important, at least in bridgehead C−H sites, for a suitable correlation of experimental C−H couplings with carbon orbital hybridization. The relationships obtained, particularly eq 26, which includes natural atomic charges along with hybridization at carbon, can be used to easily predict one-bond C−H coupling constants at tertiary sites in polycyclic saturated hydrocarbons with experimentally useful accuracy. Equations 29−30 offer simplified, more physically understandable alternatives for predictions of $^{1}J_{^{13}\mathrm{C}-^{1}\mathrm{H}}$ values from modest computational data. Their use is limited, however, by the poor performance of the PM3 model in situations like **37a**, and similar cases should be treated with caution. (4) The overall agreement of calculated with experimental data confirms that the Fermi contact interaction, as modulated by hybridization, is the dominant factor in determining the magnitude of the coupling between directly bonded carbon and hydrogen atoms. The polarity of C−H bonds, however, cannot be ignored even in hydrocarbons.

## Experimental Section

Bicyclo[3.3.1]nonane **35** was synthesized from bicyclo[3.3.1]-nonan-9-one[46] by Clemmensen reduction with amalgamated zinc and hydrochloric acid.[47] Ring expansion of bicyclo[3.3.1]-nonan-9-one with methanolic diazomethane gave bicyclo[3.3.2]-decan-9-one,[48] which was reduced under Wolff−Kishner conditions to afford bicyclo[3.3.2]decane **36**.[49] Bicyclo[3.3.3]-undecane **38** was prepared from bicyclo[3.3.1]nona-9-one by a modified synthesis following Leonard et al.[50] Physical and spectroscopic data of **35**, **36**, and **38** were in agreement with those reported in the literature.

Bicyclo[3.3.1]nonane **35**: mp 144−146 °C; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 1.78−1.94 (m, 4H), 1.6−1.68 (m, 8H), 1.45−1.55 (m, 4H); $^{13}C$ NMR (300 MHz, $CDCl_3$) $\delta$ 35.01, 31.59, 27.89, 22.52; MS(EI) *e/z* $C_9H_{16}$ 124 ($M^+$), 109, 96, 81 (base), 67, 55, 41.

Bicyclo[3.3.2]decane **36**: mp 177−179 °C; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 2.25−2.35 (m, 2H), 1.4−1.75 (m, 16H); $^{13}C$ NMR (300 MHz, $CDCl_3$) $\delta$ 33.67, 32.87, 30.36, 22.78; MS-(EI) *e/z* $C_{10}H_{18}$ 138 ($M^+$), 123, 110, 95, 81, 67 (base), 55, 41, 39.

Bicyclo[3.3.3]decane **38**: mp 191 °C; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 2.38 (m, 2H), 1.41−1.55 (m, 18H); $^{13}C$ NMR (300 MHz, $CDCl_3$) $\delta$ 30.74, 28.96, 20.1; MS(EI) *e/z* $C_{11}H_{20}$ 152 ($M^+$), 124, 109, 96 (base), 81, 67, 55.

Melting points were measured with a Thomas Hoover capillary melting point apparatus and were uncorrected. $^1H$ and $^{13}C$ NMR spectra were recorded on a Varian FT-NMR 300 MHz at ambient temperature and were referenced to solvent signals. Mass spectra were obtained using a GC−MS system consisting of a Hewlett Packard 5890 gas chromatograph interfaced to a VG Trio-1 mass spectrometer. The $^{13}C$ NMR spectrum of bicyclo[3.3.2]decane **36** is reported here for the first time, and assignments to the corresponding carbons are made based on its HMQC ($^1H$-detected heteronuclear multiple quantum coherence)[51] spectrum. Overlap of signals in the off-resonance decoupled spectra of **35** and **36** did not allow accurate measurement of the C−H direct couplings, and thus, they were obtained from the corresponding 2D heteronuclear *J*-resolved spectra.[52] The $^{13}C-^{1}H$ spin−spin coupling constants in bicyclo-[3.3.3]undecane **38** were determined from the off-resonance proton decoupled spectrum of **38**. All 2D NMR spectra were recorded on a Varian VXR 500 MHz spectrometer at 25 °C.

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**Supporting Information Available:** Selected PM3 and HF/6-31G* geometrical parameters, atomic orbital coefficients for carbon and hydrogen in the C−H bonding MO, C−H bond orders, and atomic charges for the bridgehead sites in **1**−**38** (13 pages). Ordering and accessing information is given on any current masthead page.

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(39) The linear correlation of $^1J_{^{13}C\text{-}^1H}$ with $b$, the PM3 atomic orbital coefficient on carbon (see eq 3), gives a standard deviation of 4.9 Hz.

(40) The PM3 $q_C$ and $q_H$ values for the *in*-C−H bond in bicyclo[4.4.4]-tetradecane **38a** are calculated much higher than for other bridgehead sites with similar hybridization at carbon, while at the HF/6-31G* level of calculation this discrepancy is considerably reduced. Similarly, *in*-[$3^{4,10}$]-[7]metacyclophane (see: Pascal, R. A., Jr.; Grossman, R. B.; Van Engen, D. *J. Am. Chem. Soc.* **1987**, *109*, 6878), a compound not formally included in our series since it contains aromatic carbons, gives an anomalous analysis like that of **37a**. The implication of this comparison is that the PM3 $q_C$ and $q_H$ values for **37a** might be artifactual. Other methods of charge assignment such as electrostatic potential or Mulliken population analysis do not lead to such strikingly abnormal values for these sites. When **37a** is included in the correlation, the standard deviation of the linear dependence of C−H couplings against $q_H$ is 8.3 Hz, while vs $q_C$ is 14.4 Hz (61 data points). It makes sense that $q_H$ gives a better fit, since $q_C$ has contributions from the other bonds to C as well.

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