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^{13}C, ^{1}H Spin–Spin Coupling

X*—Norbornane: A Reinvestigation of the Karplus Curve for $^{3}J(^{13}C, ^{1}H)$†

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^{13}C, ^{2}H spin–spin coupling constants over one, two and three bonds were measured from the 100-MHz ^{13}C NMR spectra of deuteriated isotopomers of norbornane-d_1 (1) and fenchane-2-d_1 (2) and also of a number of monodeuteriated alkyl-substituted adamantanes. The magnitudes of the corresponding $J(^{13}C, ^{1}H)$ values derived from these data by application of the well known relationship $J(X, ^{1}H) = 6.5144J(X, ^{2}H)$ are discussed with respect to the structural data for the hydrocarbons, which were taken from force field calculations with the Allinger MM2 method. In particular, the dihedral angle dependence and the Karplus curve for $^{3}J(^{13}C, ^{1}H)$ are investigated. Coupling constants calculated by the FP–INDO method are compared with the experimental data, and the effect of substitution by additional CC bonds in α-, β- and γ-positions of the ^{13}C-α—C-β—C-γ—H bond fragment is elucidated. If substituent effects that arise through branching and methyl substitution in 1 and 2 are taken into account for dihedral angles $\phi > 90°$, one derives $^{3}J(^{13}C, ^{1}H) = 4.50 - 0.87 \cos\phi + 4.03 \cos 2\phi$ with $J(0°) = 7.7$, $J(60°) = 2.0$ and $J(180°) = 9.4$ Hz.

KEY WORDS Karplus curve ^{13}C, ^{1}H spin–spin coupling Vicinal coupling

INTRODUCTION

The potential of ^{13}C, ^{1}H spin–spin coupling constants as powerful parameters for the elucidation of structure, conformation and stereochemistry in organic and bioorganic chemistry is well known and a number of empirical correlations between the magnitude of these coupling constants and chemical structure have been established.[2] From the various classes of $J(^{13}C, ^{1}H)$ data observed experimentally, those over one and three bonds, $^{1}J(^{13}C, ^{1}H)$ and $^{3}J(^{13}C, ^{1}H)$, respectively, are by far the most important. While $^{1}J(^{13}C, ^{1}H)$ data are primarily of diagnostic value for carbon hybridization in hydrocarbons,[3] vicinal ^{13}C, ^{1}H interactions are essential parameters for stereochemical analysis.[2a,2d,4] A prominent aspect in this context is the dihedral angle (ϕ) dependence of $^{3}J(^{13}C, ^{1}H)$ data, which shows the general behaviour described by Karplus for $^{3}J(^{1}H, ^{1}H)$ couplings:[5] Large values for $\phi = 0°$ and 180° and small values for $\phi \approx 90°$.

Over the years, the dihedral angle dependence of vicinal ^{13}C, ^{1}H coupling constants has been intensively studied and several attempts to establish Karplus curves for these parameters in ^{13}CCC^{1}H, ^{13}CNC^{1}H, and ^{13}COC^{1}H bond fragments (the last two of primary interest in the field of peptides, nucleosides or nucleotides and oligosaccharides, respectively) have been published.[6–28] Nevertheless, only limited data are available for rigid hydrocarbons with well defined torsional angles. Our own investigations of scalar ^{13}C,^{1}H couplings in this field have dealt with adamantane, where information about the angular dependence of vicinal ^{13}C, ^{1}H coupling constants and the influence of the substitution pattern on the magnitude of these parameters was obtained.[29,30] In addition to a torsional angle dependence for $^{3}J(^{13}C, ^{1}H)$, these data indicated that γ-substitution in the ^{13}C-α—C-β—C-γ—^{1}H fragment by a methylene or methyl group reduces the coupling by about 1–2 Hz, a finding in accord with the predictions of MO theory.[31]

This paper extends this work to norbornane (1) and fenchane (2), other rigid molecules suitable as model systems for the investigation of stereochemical factors important for indirect NMR spin–spin coupling constants. Indeed, norbornane and its derivatives have been used frequently for studies in the field of ^{1}H, ^{1}H, ^{1}H, ^{19}F, ^{13}C, ^{13}C, ^{13}C, ^{19}F and ^{13}C, ^{31}P coupling constants,[32] and a preliminary report on results for 1 from this laboratory[33] already demonstrated a Karplus-type behaviour for the $^{3}J(^{13}C, ^{1}H)$ values in this compound. In addition, we investigated specific coupling pathways in a number of substituted adamantanes (3, 4, R = C_2H_5, $n-C_3H_7$, C_6H_5). The major goal of the present investigation was to establish a quantitative expression for the dihedral angle dependence of $^{3}J(^{13}C, ^{1}H)$ in hydrocarbons and to elucidate the influence of additional CC bonds in the ^{13}C—C—C—^{1}H fragment on $^{3}J(^{13}C, ^{1}H)$.

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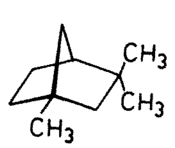

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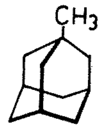

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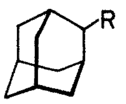

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* For Part IX, see Ref. 1.

† Dedicated to Professor W. von Philipsborn on the occasion of his 60th birthday.

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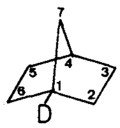
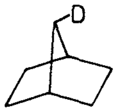
RESULTS

The large number of spins prevents a complete analysis of the norbornane spectrum in terms of ^1H, ^1H and ^{13}C, ^1H coupling constants.[32a] The use of substituted systems, on the other hand, complicates the interpretation of the results owing to the existence of additional substituent effects for the coupling constants of interest. In an attempt to minimize these perturbations and at the same time to simplify the experimental determination of ^{13}C, ^1H coupling constants, we have again decided to investigate the ^{13}C, ^2H coupling constants using suitable deuteriated isotopomers.[34] For this purpose the isomeric monodeuteriated norbornanes **1a–d** were synthesized and their ^{13}C, ^2H coupling constants measured from the $^{13}C\{^1H\}$ NMR spectra.



1a



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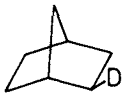

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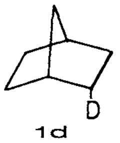

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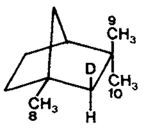
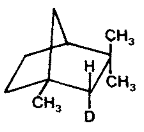


2a



2b

Owing to the isotope effect on ^{13}C chemical shifts,[35] resonances that are otherwise degenerate are well resolved at high B_0 field and line splittings which exceed 0.5 Hz can easily be determined.[36] The results are summarized in Table 1. On the basis of the well established equation[37]

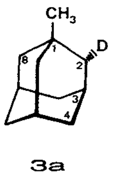
$$^nJ(^{13}C,^1H) = (\gamma_H/\gamma_D)^nJ(^{13}C,^2H) = 6.5144\,^nJ(^{13}C,^2H) \qquad (1)$$

the measured data were transformed into the corresponding $^1J(^{13}C, ^1H)$ values. The coupling constants derived in this way are given in Table 2.

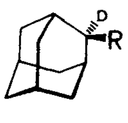
During the investigation of the dihedral angle dependence of $^3J(^{13}C, ^1H)$, it became apparent that experimental data for $\phi = 0°$ were desirable. Since none of the bond fragments in norbornane yields this value (in fact, for a saturated cyclic system a CCCH fragment with $\phi = 0°$ is highly unlikely), the fenchane-2-d_1 isotopomers **2a** and **2b** were synthesized and their ^{13}C NMR spectra analyzed as described for **1a–d**. These results are also given in Tables 1 and 2.

Further, because the $^{13}C—C—C—^1H$ fragments of interest for $^3J(^{13}C, ^1H)$ values in norbornane display various substitution patterns which may, according to theory[31] and experiment,[29,30] influence the magnitude of the spin–spin coupling constants, a detailed consideration of this effect seemed desirable. For this purpose, the substituted adamantanes **3a** and **4a** ($R = C_2H_5$, n-C_3H_7, C_6H_5) were synthesized and their ^{13}C, ^2H coupling constants measured. These data are given in Table 3.

Owing to the unfavourable γ_D/γ_H ratio, not all of the ^{13}C, ^2H splittings could be resolved. Further com-



3a



4a

Table 1. ^{13}C, ^2H spin–spin coupling constants of isotopomers **1a–d**, **2a** and **2b** (Hz)

Compound	Carbon	n[a]	$^nJ(^{13}C, ^2H)$	Compound	Carbon	n[a]	$^nJ(^{13}C, ^2H)$[c]
1a	C-1	1	21.55 ± 0.06	**2a**	C-1	2	0.48
	C-3	3	1.06 ± 0.04		C-2	1	19.40
	C-4	3	1.31 ± 0.06		C-3	2	0.59
					C-6	3	1.11
1b	C-7	1	20.17 ± 0.07		C-7	3	—
	C-2, 3	3	0.34[b]		C-8	3	0.39
	C-5, 6	3	1.31 ± 0.07		C-9	3	1.23
					C-10	3	—
1c	C-1	2	0.48 ± 0.04				
	C-2	1	19.78 ± 0.02	**2b**	C-1	2	0.44
	C-3	2	0.61 ± 0.03		C-2	1	19.87
	C-4	3	0.16[b]		C-3	2	—
	C-6	3	1.34 ± 0.02		C-6	3	0.75
					C-7	3	1.07
1d	C-1	2	0.49 ± 0.05		C-8	3	—
	C-2	1	20.11 ± 0.04		C-9	3	—
	C-3	2	0.22 ± 0.04		C-10	3	0.89
	C-4	3	0.34 ± 0.05				
	C-6	3	0.81 ± 0.05				
	C-7	3	1.09 ± 0.05				

[a] Number of bonds.
[b] Determined by line-shape analysis.
[c] Digital resolution 0.04 Hz per point.

Table 2. ${}^{13}C$, ${}^{1}H$ coupling constants (Hz) for norbornane (1) and fenchane (2) calculated from the data in Table 1 by Eqn (1); dihedral angles, ϕ, for vicinal couplings in degrees

	One-bond coupling					Geminal coupling[a]			
	1, 1	2, 2_{ex}	2, 2_{en}	7, 7		1, 2_s	1, 2_{en}	3, 2_{ex}	3, 2_{en}
1	140.4	128.9	131.0	131.4		(−) 3.1	(−) 3.2	(−) 4.0	(−) 1.4
2	—	126.4	129.4	—		(−) 3.1	(−) 2.9	(−) 3.8	—
					Vicinal coupling				
	3, 1	4, 1	2, 7_s	2, 7_a	4, 2_{ex}	4, 2_{en}	6, 2_{ex}	6, 2_{en}	7, 2_{en}
1	6.9	8.5	2.2	8.5	1.0	2.2	8.7	5.3	7.1
ϕ	161	180	60	173	118	121	170	50	158
	6, 2_{ex}	6, 2_{en}	7, 2_{en}	8, 2_{ex}	9, 2_{ex}	10, 2_{en}			
2	7.2	4.9	6.9	2.5	8.0	5.8			
ϕ	172	53	161	44	2	2			

[a] Negative sign assumed.

Table 3. ${}^{13}C$, ${}^{2}H$ coupling constants (Hz)[a] for substituted adamantanes-2-d_1 3a and 4a ($R = C_2H_5$, n-C_3H_7, C_6H_5); ${}^{n}J({}^{13}C, {}^{1}H)$ values (Hz, italics) derived from Eqn (1)

Compound	C-2 (${}^1J$)	C-1 (${}^2J$)	C-3 (${}^2J$)	C-4 (${}^3J$)	C-8 (${}^3J$)	CH_3 (${}^3J$)	α-CH_2(${}^2J$)
3a[b]	19.30	(−) 0.51	(−) 0.49	1.12	0.98	0.31	—
	125.73	(−) *3.32*	(−) *3.19*	*7.29*	*6.38*	*2.02*	—
4a ($R = C_2H_5$)	19.14[c]	(−) 0.54[d]	—	0.81[d]	—	—	(−) 0.56[d]
	124.69	(−) *3.52*	—	*5.28*	—	—	(−) *3.65*
4a ($R = n$-C_3H_7)	19.12[d]	(−) 0.61[e]	—	0.82[e]	—	—	(−) 0.45[b]
	124.56	(−) *3.97*	—	*5.54*	—	—	(−) *2.93*
4a ($R = C_6H_5$)	19.26[d]	—	—	0.79[d]	—	—	(−) 0.93[d,f]
	125.47	—	—	*5.15*	—	—	(−) *6.06*

[a] Digital resolution/error in ${}^{n}J$(C, H).

[b] 0.02/0.16.

[c] 0.10/0.65.

[d] 0.05/0.33.

[e] 0.06/0.39.

[f] C-1.

plications arose in a few cases from fast deuterium quadrupolar relaxation that can lead to line broadening and systematic errors in the measured line splittings. Pople[38] has treated this effect theoretically and, on the basis of his theory, an empirical correction was employed, where necessary. For this purpose we determined the ${}^{2}H$ spin–lattice relaxation times T_1 for **1a–d** by the inversion–recovery method.[39] The correction procedure then used is described in more detail under Experimental.

Another source of systematic errors in this type of investigation is the possibility of primary isotope effects on ${}^{n}J({}^{13}C, {}^{2}H)$ values. This problem has been tackled by various workers, mainly for one-bond couplings, but in most cases the observed changes were just within experimental error.[40] Nevertheless, in agreement with a theoretical study,[41] the experimental data indicate a possible negative primary ${}^{2}H/{}^{1}H$ isotope effect of <0.5%. More recently, Everett[42] has established such data by accurate measurements for a number of simple systems. We have determined the primary isotope effect on ${}^{1}J({}^{13}C, {}^{2/1}H)$ in chloroform and the sum of the primary and secondary isotope effect on ${}^{1}J({}^{13}C, {}^{2,1}H)$ in methylene chloride independently, and our results (Table 4) are in perfect agreement with those recorded by Everett, even if the absolute values for the coupling constants differ owing to the different experimental conditions (cf., Experimental). Further, a primary isotope effect for ${}^{1}J({}^{13}C, {}^{2/1}H)$ in acetylene was reported by Luzikov and Sergeyev.[43] They found a reduction of 0.64 Hz when ${}^{1}J({}^{13}C, {}^{1}H)$ calculated from ${}^{1}J({}^{13}C, {}^{2}H)$ on the basis of Eqn (1) was compared with the experimental ${}^{1}J({}^{13}C, {}^{1}H)$ value. This corresponds to a primary isotope effect of −0.25%. A realistic estimate for the upper limit of the expected primary isotope effect on ${}^{1}J({}^{13}C, {}^{1}H)$ is therefore −0.5%.

Table 4. One-bond ${}^{13}C$, ${}^{2}H$ and ${}^{13}C$, ${}^{1}H$ coupling constants for deuteriated and non-deuteriated chloroform and methylene chloride, respectively, and primary isotope effect ΔJ (Hz) $= {}^{1}J_{calc} - {}^{1}J_{exp}$ [${}^{1}J_{calc}$ From Eqn (1)]

Compound	${}^1J_{exp}$	${}^1J_{calc}$	$\Delta{}^1J$
$CDCl_3$	$32.14 \pm 0.02_5$		
$CHCl_3$	210.36 ± 0.05	209.39 ± 0.16	-0.97 ± 0.17
CD_2Cl_2	$27.27 \pm 0.01_5$		
CH_2Cl_2	178.54 ± 0.03	177.66 ± 0.10	-0.88 ± 0.10

For ${}^{n}J({}^{13}C, {}^{2}H)$ with $n > 1$, the primary isotope effects observed so far were mostly smaller than the experimental error.[40] Hansen and Led[44] reported for the first time a sizable primary isotope effect for long-range ^{13}C, $^{2/1}H$ coupling constants in cyclobutene (in one case *ca.* 5%), but a study by Sergeyev[40] on benzaldehyde again yielded a value of only 1% for $^3J(^{13}C, ^{2/1}H)$. With this in mind, and the reasonable assumption that the magnitude of the isotope effect should reflect the magnitude of the particular coupling constant, it seems justified, considering the relatively large experimental error that results through the use of eqn (1), to neglect primary $^2H/^1H$ isotope effects for coupling constants over more than one bond in the following discussion.

The structural data used for **1** and **2** were derived from force field calculations with the Allinger MM2 model.[45] The experimental carbon geometry of **1** as determined by a joint analysis of several experimental and theoretical data sets[46] is in reasonable agreement with these results. Some improvements have recently been obtained with the new MM3 force field,[47] notably for the C-2—C-3 bond length (MM2 154.1, MM3 155.7, exp. 155.9–157.3 pm) and the C-1—C-7—C-4 bond angle (MM2 92.5°, MM3 95.0°, exp. 93.4–94.6°), but the CCCC torsional angles given by the two force fields are not very different. We also can conclude from our MNDO results for **1**,[35] which yield the improved C-2—C-3 bond length of 155.7 pm, that the CCCH torsional angles, which are of primary interest in the present context, are not much affected by small bond length variations. Since for the hydrogen locations the experimental work does not yield independent results, and neither an experimental nor an MM3 geometry is available for **2**, we decided to use MM2 results throughout. In addition, there is good reason to believe that the effect of the differences in the CCCH dihedral angles derived from the various computational methods on the ^{13}C, ^1H coupling constants is much smaller than the experimental error of our measurements.

DISCUSSION

^{13}C, ^1H coupling constants over one and two bonds

The measured $^1J(^{13}C, ^2H)$ data and the calculated $^1J(^{13}C, ^1H)$ values for norbornane (Tables 1 and 2, respectively) reflect the well known dependence of these parameters on the s character of the CH bond hybrids; this may differ considerably for the various CH bonds in saturated bicyclic systems. The data for **1** from the older literature[48] are in agreement with our values, but suffer from larger experimental errors (up to 2 Hz).

For **2**, the $^1J(^{13}C, ^1H)$ values determined at C-2 for the *exo*- and *endo*-CH bonds via the isotopomers **2a** and **2b** are smaller by 2.5 and 1.6 Hz, respectively, than the corresponding data for **1** (Table 2). Hence the s character in the CH bond hybrids of **2** is slightly reduced, presumably a consequence of the electron-releasing effect of the methyl groups.

The sign information for the geminal interactions is not available from our results, but a negative sign can be assumed on the basis of other experimental evidence.[2] The values observed for **1** are similar in magnitude to those in other saturated systems, but there is a distinct difference between the $^2J(2, 3_{ex})$ and $^2J(2, 3_{en})$ couplings. This is not surprising, however, since other parameters are also different for *endo*- and *exo*-protons. Among these are the $^1J(^{13}C, ^1H)$ values (see Table 2), the $^3J(^1H, ^1H)_{cis}$ coupling constants[49] and the ^1H chemical shifts.[49] Compared with $^2J(1, 2_{ex})$ and $^2J(1, 2_{en})$, $^2J(3, 2_{ex})$ is increased by 0.8 Hz, while $^2J(3, 2_{en})$ is decreased by 1.8 Hz. Since $^2J(1, 2_{ex})$ and $^2J(1, 2_{en})$ are identical within experimental error, the different s character in the CH_{ex} and CH_{en} bond cannot be responsible for the observed effect. The same is true for a possible difference in CCH bond angles, which has been reported to influence the magnitude of geminal ^{13}C, ^1H coupling constants in unsaturated systems.[50] According to our MM2 results, only small variations exist for the relevant parameters ($\angle$C-1—C-2—H_{ex} = 111.0°; $\angle$C-1—C-2—H_{en} = 112.8°; $\angle$C-2—C-3—H_{ex} = 111.6°; $\angle$C-2—C-3—H_{en} = 112.3°). Other, yet unknown factors must therefore be involved. For $^3J(^1H, ^1H)$ it has been shown theoretically that the difference between *endo,endo* and *exo,exo* spin–spin couplings results from non-bonded interactions between the C-7 methylene group and the C-2—C-3 bond fragment[49] which strongly reduce the *endo,endo* interaction. A similar mechanism may also be important for $^2J(^{13}C, ^1H)$.

The geminal couplings in the C-1—C-2 fragment of **2** are, within experimental error, identical with those in **1**. The same is true for $^2J(3, 2_{ex})$, whereas $^2J(3, 2_{en})$ was not resolved and is presumably smaller than the analogous interaction in **1**.

Vicinal ^{13}C, ^1H interactions

If bond length and bond angle variations are small, the dominating factor that determines vicinal spin–spin interactions in hydrocarbons is the torsional angle dependence predicted by Karplus[5] and Conroy[51] for ^1H, ^1H coupling constants, and later also found for a large variety of other nuclei in a vicinal arrangement.[2b,d] Whereas Karplus curves for $^3J(^1H, ^1H)$ and other pairs of nuclei are in widespread use, the torsional angle dependence of $^3J(^{13}C, ^1H)$ data, first observed experimentally by Lemieux *et al.*[6] and shortly afterwards predicted theoretically for propane by Wasylishen and Schaefer,[8] has found a more limited application. Experimental attempts to derive a Karplus curve for $^3J(^{13}C, ^1H)$ have been reviewed,[2] and these results support a general Karplus-type behaviour also for this coupling. With respect to a quantitative picture, however, some of the earlier experimental investigations suffer from the fact that substituted systems were studied, where additional complications due to electronegative groups[20,23,52,53] exist. For example, in the case of **2** a comparison for $^3J(10, 2_{en})$ is possible with the corresponding coupling constant measured by Spoormaker and de Bie[17] for 2-*endo*-methyl-2-bornanol (5.25 Hz), which is 0.6 ± 0.2 Hz smaller than the value we found for **2b** (Table 2). A reinvestigation of this problem with data confined to hydrocarbons was thus of interest.

Before starting our analysis, however, it seems appropriate to emphasize that the ideal system for the isolation of the dihedral angle dependence of $^3J(^{13}C, ^1H)$ is not available, since even rigid hydrocarbons such as **1** and **2** have a number of additional features that may influence the magnitude of vicinal ^{13}C, ^1H coupling constants. In this respect, the following aspects have to be considered:

i. Coupling constants in cyclic systems can be transmitted by multiple pathways, and the measured data may correspond to a cumulative effect of the type $J_{obs} = {}^nJ + {}^{(n+1)}J + {}^{(n+2)}J$, etc.

ii. While strong perturbations by electronegative substituents are absent, theory[31] and experiment[29,30,52] have shown that $^3J(^{13}C, ^1H)$ data are subject to changes due to the introduction of alkyl groups. Thus, a methyl group in γ-position at the ^{13}C-α—C-β—C-γ—^1H fragment will reduce the corresponding $^3J(^{13}C, ^1H)$ value by 1.0–2.0 Hz. Further, this effect itself shows a dihedral angle dependence.[20]

iii. In strained systems such as **1** and **2**, the effect of ring strain may alter the $^3J(^{13}C, ^1H)$ data in an unforeseen manner. Although it is difficult or even impossible to account for the diffuse aspect of 'strain effects' in a concise and logical manner, alterations for both the CCC and the CCH bond angles may be used to obtain access to this information.

Notwithstanding these reservations, an analysis of the $^3J(^{13}C, ^1H)$ values from Table 2 is shown in Fig. 1, where the dihedral angles for **1** and **2** are taken from the MM2 results. Clearly, the familiar behaviour is found and the experimental data, fitted by Eqn (2), are in good agreement with the Karplus curve derived from MO calculations for propane[8,20] [Eqn (3) and broken line in Fig. 1].

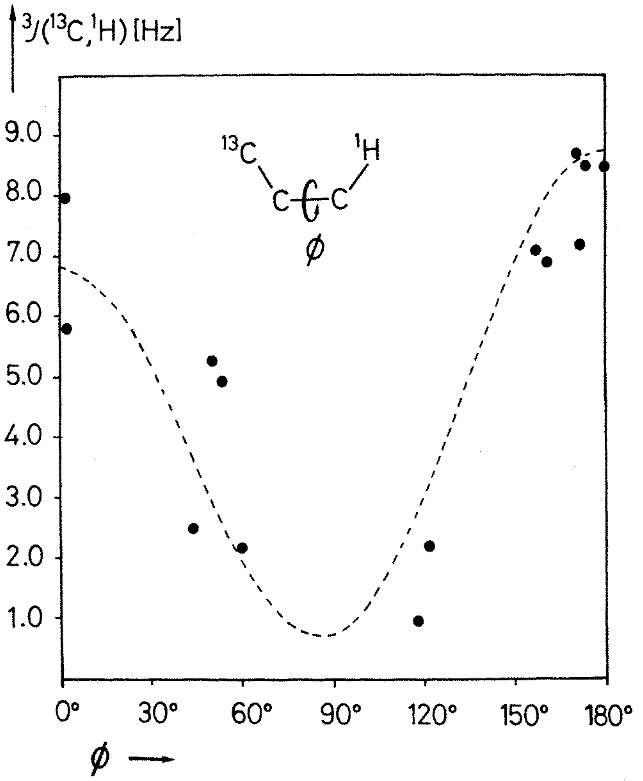


Figure 1. Plot of experimental $^3J(^{13}C, ^1H)$ coupling constants of **1** and **2** (Hz; cf. Table 2) against the dihedral angles ϕ (MM2 results) of the respective ^{13}C—C—C—^1H bond fragments and theoretical Karplus curve, Eqn (3) (broken line).

$$^3J(^{13}C, ^1H) = 4.19 - 0.27 \cos \phi + 3.52 \cos 2\phi \quad (2)$$

$$[J(0°) = 7.44,\ J(60°) = 2.30,\ J(180°) = 7.98\ \text{Hz}]$$

$$^3J(^{13}C, ^1H) = 4.26 - 1.00 \cos \phi + 3.56 \cos 2\phi \quad (3)$$

$$[J(0°) = 6.82,\ J(60°) = 1.98,\ J(180°) = 8.82\ \text{Hz}]$$

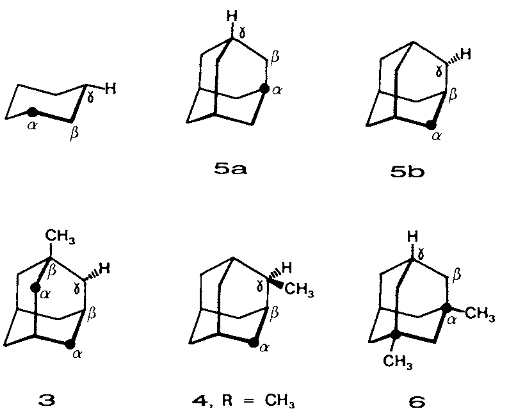
It is also of interest that for cyclohexane as an unstrained system, $^3J(^{13}C, ^1H)$ values of 2.12 and 8.12 Hz (experimental error 0.05 Hz) have been measured[54] for $\phi = 60°$ (^3J_g) and $\phi = 180°$ (^3J_t). These data compare favourable with $^3J(2, 7_s)$ and $^3J(4, 1)$, respectively, in **1** (Table 2). We note, however, that the $^3J_{cis}/^3J_{trans}$ ratio from Eqn (2) is large (0.93). Further, in analogy with the other findings discussed above, there is again a large difference between the *exo* and *endo* coupling at the C-2—C-3 fragment, $^3J(9, 2_{ex})$ and $^3J(10, 2_{en})$. Also, the two $^3J(6, 2_{en})$ values for **1** and **2** are much larger than other couplings with a similar dihedral angle, and for **1** $^3J(4, 2_{en})$ is twice as large as $^3J(4, 2_{ex})$, despite only a minor difference in the ϕ values.

The additional factors that might influence the $^3J(^{13}C, ^1H)$ data in **1** and **2**, as listed above, are now discussed. As far as multiple pathways are concerned, we were not able to resolve $^4J(^{13}C, ^2H)$ coupling constants in cases where a single four-bond pathway exists, as for C-5 in **1c** and **1d** as well as in the isotopomers **2a** and **2b**. It seems justified, therefore, to conclude that ^4J contributions in the present case are significantly smaller than 1 Hz and that multiple pathways for the $^3J(^{13}C, ^1H)$ data can be neglected.

Deviations of internal CCC or CCH bond angles from 'normal', i.e. close to tetrahedral, values are certainly present in both hydrocarbons, but an inspection of the structural data reveals no clear trend for the various $^3J(^{13}C, ^1H)$ data. For instance, the most pronounced reduction for the CCC angle in one of the CCCH bond fragments under consideration is found for $^3J(4, 1)$, with a value of 92.5° at C-7. The coupling constant does not, however, deviate much from the other ^3J values where similar dihedral angles apply, as for instance $^3J(2, 7a)$ or $^3J(2, 6_{ex})$. Also, the agreement with the cyclohexane data mentioned above does not indicate any 'strain effect'.

We are then left with the consequence of substitution by alkyl groups. The incorporation of a particular ^{13}C—C—C—^1H fragment into a bicyclic ring system means that additional C—C bonds lead to chain prolongation and branching. In order to analyse this aspect, we consider adamantane data, where several substitution patterns are available. For this purpose, the relevant structures, together with cyclohexane as reference compound, are summarized in Scheme 1. The comparison is based on our results for the parent system adamantane[29] (**5a**, **5b**) and for the substituted systems 1-methyladamantane (**3**, Table 3), 2-methyladamantane[30] (**4**, R = CH_3), and 3,5-dimethyladamantane[30] (**6**). All coupling pathways considered involve a transoid bond arrangement (ϕ = 180°).

If we first consider the data for **4a** (R = CH_3) and for the series **4a** (R = C_2H_5, n-C_3H_7, C_6H_5) (Table 3), we



Scheme 1

find that chain prolongation in the γ-position does not alter the coupling significantly. Thus, the effect of the first CC bond dominates. With this in mind and cyclohexane as a reference, which already accounts for the fact that any coupling path in a cyclic system involves one α- and one γ-effect, we can extract from the diagram Table 5 for the additional pattern of α-, β- and γ-substitution by a CC bond.

A straightforward analysis of these data yields $+0.2 \pm 0.4$ Hz for the α-effect, -0.9 ± 0.3 Hz for the β-effect and -1.7 ± 0.5 Hz for the γ-effect. The last result is in excellent agreement with predictions from MO theory, where model calculations for alkanes yielded a γ-effect of -1.0 Hz.[31] The calculated α-effect was small and negative, and no significant β-effect was found.[20,52] Since we find the α-effect to be zero within experimental error, only the observed β-effect is, as already noted,[20] at variance with the MO results, but supported by the experimental data for 2-substituted propanes.[52]

Table 5. Additional pattern of α-, β- and γ-substitution by a CC bond

Compound	α	β	γ	$^3J(^{13}C, ^1H)$ (Hz)
C_6H_{12}	—	—	—	8.12 ± 0.05
5a	1	—	1	5.57 ± 0.16
5b	—	1	—	7.17 ± 0.39
3	—	1	—	7.29 ± 0.16
	—	2	—	6.38 ± 0.16
4a (R = CH_3)	—	1	1	5.57 ± 0.40
6	2	—	1	5.77 ± 0.40

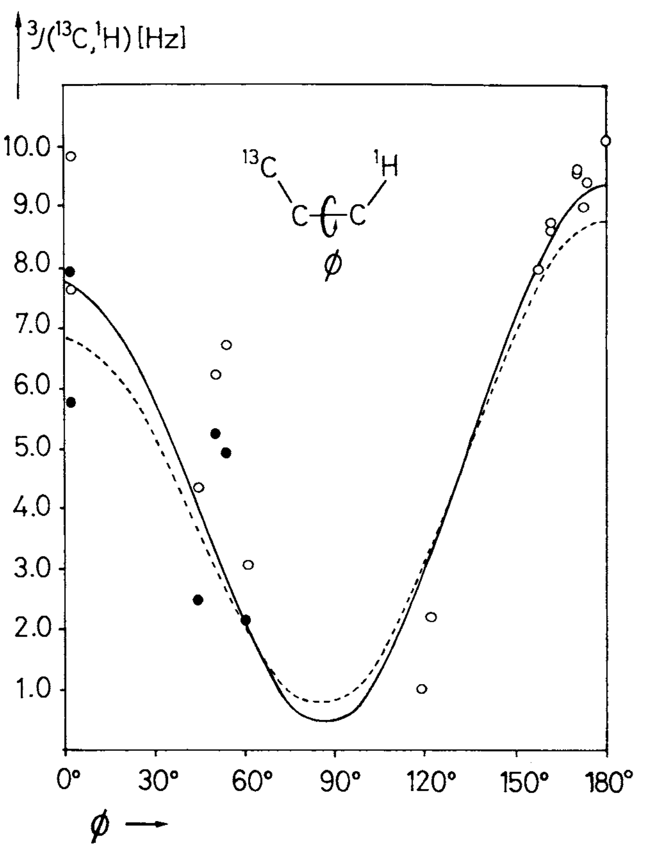


Figure 2. $^3J(^{13}C, ^1H)$ vs. ϕ plot as in Fig. 1 with coupling constants corrected for substitution and branching (open symbols) and uncorrected values for $\phi < 90°$ (filled symbols). Theoretical Karplus curve, Eqn (3) (broken line), and experimental Karplus curve Eqn (4) (solid line).

If we assign the substituent effects from the adamantane analysis to the various vicinal ^{13}C, ^1H coupling constants in **1** and **2** in order to account for branching and methyl substitution, corrected coupling constants result, as shown in Table 6 and Fig. 2. Clearly, in the light of the previous findings[6–28] and the ratio of 0.60 reported for $^3J_{cis}/^3J_{trans}$ in propene,[55] the new points lead to an unrealistically large $^3J_{cis}/^3J_{trans}$ ratio (0.99). One also notes that the differences for the *exo*/*endo* pairs discussed above prevail. They must, therefore, be attributed to electronic effects inherent in the bicyclic structure and cannot be traced to the substitution pattern.

A further analysis of the substituent effect is possible with the data for **1c** and **d** and **2a** and **b** because methyl

Table 6. Vicinal ^{13}C, ^1H coupling constants (Hz) in 1 and 2 corrected for substitution effects (A) and Calculated by the FP-INDO method (B), and (C) dihedral angles, ϕ, in degrees

Parameter	3, 1	4, 1	2, 7_s	2, 7_a	4, 2_{ex}	4, 2_{en}	6, 2_{ex}	6, 2_{en}	7, 2_{en}	7, 2_{ex}
A	8.6	10.2	3.1	9.4	1.0	2.2	9.6	6.2	8.0	—
B	8.62	11.59	1.60	9.34	1.79	3.75	8.09	4.14	8.44	0.40
C	161	180	60	173	118	121	170	50	158	82

Parameter	6, 2_{ex}	6, 2_{en}	7, 2_{en}	8, 2_{ex}	9, 2_{ex}	10, 2_{en}	4, 2_{ex}	4, 2_{en}	7, 2_{ex}	8, 2_{en}	9, 2_{en}	10, 2_{ex}
A	9.0	6.7	8.7	4.3	9.8	7.6	—	—	—	—	—	—
B	8.44	3.91	8.15	2.56	7.35	6.54	1.45	4.30	0.46	0.34	3.00	5.65
C	172	53	161	44	2	2	116	124	80	75	119	122

substitution in the latter compounds provides additional substituent patterns. Considering the experimental error in our $^3J(^{13}C, ^1H)$ data derived via Eqn (1), we find from the entries for the 6, 2_{ex}, 6, 2_{en} and 7, 2_{en} coupling constants in Table 2 (interactions which are resolved in both cases and subject to one β-effect) a significant β-effect only for $^3J(6, 2_{ex})$ (pair **1c**/**2a**; -1.5 ± 0.3 Hz, $\phi = 170°/172°$), whereas the coupling of C-6 to the *endo*-proton (pair **1d**/**2b**) differs only by 0.4 ± 0.3 Hz and the $^3J(7, 2_{en})$ values are the same within experimental error. The dihedral angles amount here to 50°/53° and 158°/161°, respectively. On the other hand, coupling to C-4 in **2a** and **b** is subject to two additional β-effects and, as expected if one considers the small magnitude of these couplings in **1c** and **1d** (Table 2), $^3J(4, 2_{ex})$ and $^3J(4, 2_{en})$ were not resolved in the fenchane isotopomers. Hence, although some results are in line with our analysis of the adamantane data, others are not. Therefore, a straightforward application of the data derived from the adamantane system to the norbornane skeleton seems not to be justified.

This conclusion is supported by a closer inspection of Fig. 2 that reveals systematic deviations of the points for $\phi < 90°$ from the theoretical curve (broken line). It therefore appears that the β-effect for C—C substitution derived above depends on the dihedral angle, and the increment determined from the $^3J(180°)$ data of the adamantanes **3**–**6** is adequate only for transoid couplings, but much too large for coupling pathways with $\phi < 90°$. This interpretation finds experimental support by vicinal coupling constants measured for $\phi = 60°$ ($^3J_{gauche}$) in **1**, **3** and cyclohexane, which are identical within experimental error. For $^3J(2, 7_s)$ in **1** with one β-substitution we find 2.2 Hz (Table 2), for $^3J(CH_3, H)$ in **3a** with two β-substitutions 2.0 Hz (Table 3), and for ^3J_g in cyclohexane with no β-substituent the result is 2.12 Hz.[54] Thus, the β-effect is negligible for $\phi = 60°$. In addition, calculations for the γ-effect[20] on $^3J(^{13}C, ^1H)$ yielded exactly such a dihedral angle dependence. Therefore, if we combine the corrected values for $\phi > 90°$ (Table 6) with the uncorrected values for $\phi < 90°$ (Table 2), the following equation results:

$$^3J(^{13}C, ^1H) = 4.50 - 0.87 \cos \phi + 4.03 \cos 2\phi \quad (4)$$

$$[J(0°) = 7.66, J(60°) = 2.04, J(180°) = 9.40 \text{ Hz}]$$

which is now in close agreement with Eqn (3) (Fig. 2). It also replaces Eqn (a) of our preliminary communication.[33]

It was also of interest to calculate the $^3J(^{13}C, ^1H)$ data for **1** and **2** with the well established FP–INDO method.[56] As Fig. 3 shows, there is satisfactory agreement between theory and experiment, except for $^3J(4, 1)$, where the theoretical value seems to be too large. Calculations using different geometries for **1** showed that this coupling is extremely sensitive to the C-1—C-7—C-4 bond angle and the corresponding C-1—C-4 distance, which is in line with results from theoretical investigations of several bicycloalkanes with different bridge size.[32f,1] Larger angles showed much smaller couplings (93.2°,[57] 10.07 Hz; 96°,[58] 8.59 Hz) and the MM2 results are not accurate enough to determine this parameter with the necessary precision. The larger

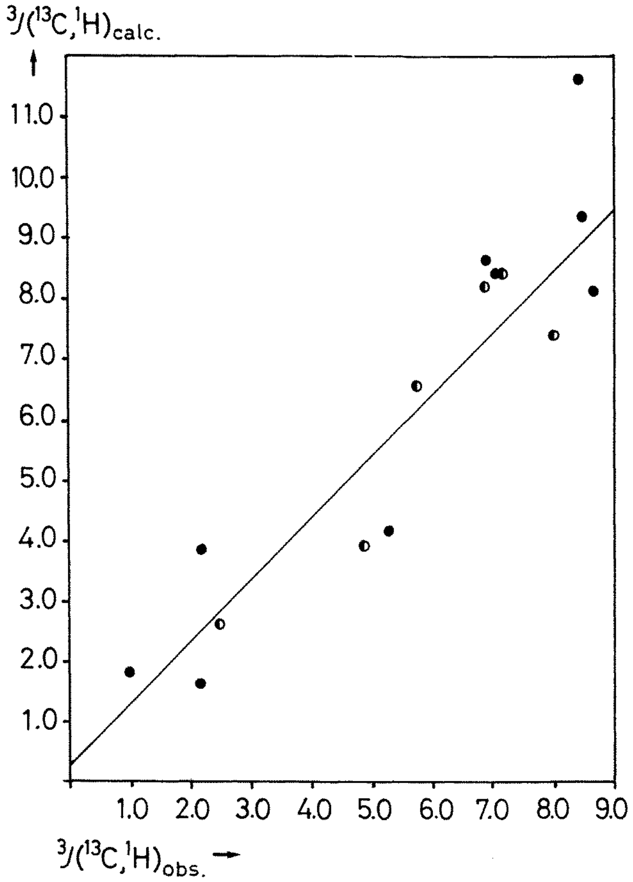


Figure 3. Comparison of calculated and observed $^3J(^{13}C, ^1H)$ data for **1** (filled symbols) and **2** (half-filled symbols); linear regression analysis yields $J_{calc} = 1.017J_{obs} + 0.302$ ($R = 0.93$); for **2**, only the data corresponding to the isotopomers **2a** and **2b** are included.

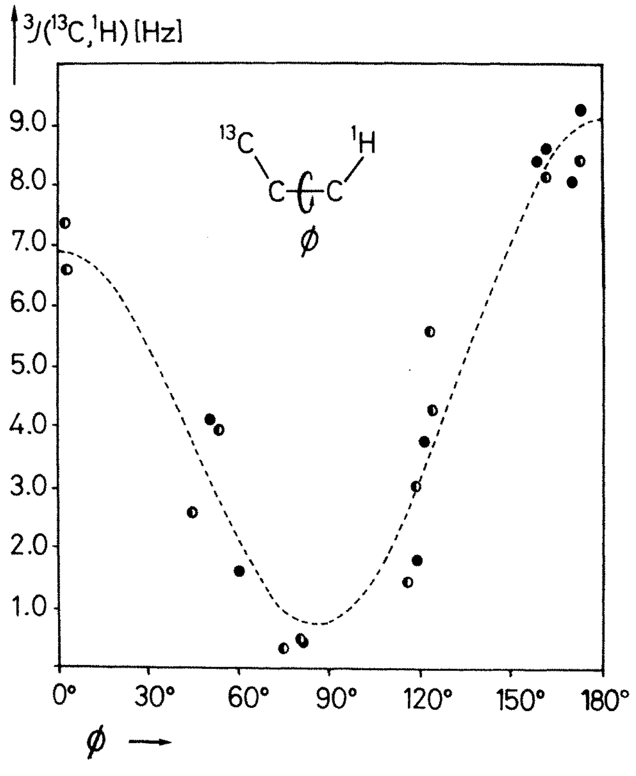


Figure 4. Plot of calculated $^3J(^{13}C, ^1H)$ values for **1** (filled symbols) and **2** (half-filled symbols) against dihedral angles ϕ; broken line, Eqn (5).

angle obtained by the MM3 force field (95.0°)[47] is expected to yield a better agreement with experiment.

A plot (Fig. 4) of the theoretical $^3J(^{13}C, ^1H)$ values (Table 6) against the corresponding dihedral angles ϕ, omitting $^3J(4, 1)$ for the reasons discussed above, again shows close correspondence with the theoretical Karplus curve for propane [Eqn (3)] and our Eqn (4). The analytical expression is

$$^3J(^{13}C, ^1H) = 4.40 - 1.11 \cos\phi + 3.65 \cos 2\phi \quad (5)$$

$$[J(0°) = 6.94, J(60°) = 2.01, J(180°) = 9.16 \text{ Hz}]$$

CONCLUSION

There is good agreement between the experimental $^3J(^{13}C, ^1H)$ data for **1** and **2** and the calculated dihedral angle dependence of these coupling constants either in propane or in both bicyclic systems. The effect of branching and/or methyl substitution in **1** and **2** is smaller than expected. Except for cases with dihedral angles in the range 90–180°, corrections of the data derived from the bicyclic systems are not required. A similar result has been obtained recently for the Karplus curve in the $^{13}C—O—C—^1H$ fragment of carbohydrates,[27,28] where the experimental Eqn (6)[27] compares favourably with Eqn (7) calculated for dimethyl ether,[8] despite several substitution patterns present in the set of compounds used to determine the experimental data:

$$^3J(^{13}C, ^1H) = 3.35 - 0.70 \cos\phi + 2.75 \cos 2\phi \quad (6)$$

$$[J(0°) = 5.40, J(60°) = 1.62, J(180°) = 6.80 \text{ Hz}]^*$$

$$^3J(^{13}C, ^1H) = 3.10 - 1.14 \cos\phi + 3.05 \cos 2\phi \quad (7)$$

$$[J(0°) = 5.01, J(60°) = 1.01, J(180°) = 7.29 \text{ Hz}]$$

We believe that the present results [Eqn (4)] form a reliable basis for dihedral angle estimates in hydrocarbons, either in connection with conformational analyses or the interpretation of cross peaks in 2D ^{13}C, ^1H shift correlation spectroscopy.[59] With the broader use of 2D techniques and better instrumentation, more experimental $^3J(^{13}C, ^1H)$ values will certainly become available from heteronuclear J-resolved experiments,[60,28] but also from fully coupled ^{13}C, ^1H correlation spectra[59,61] if better resolution can be achieved.

EXPERIMENTAL

Compounds

The synthesis of the deuteriated norbornanes **1a–d** has been described.[35] For the preparation of **2a** and **2b** fenchone (EGA-Chemie) was reduced to *endo*-2-fenchyl alcohol and *endo*-2-fenchyl alcohol-*exo*-2-d_1 with $LiAlH_4$ and $LiAlD_4$, respectively. The alcohols were transformed into the *exo*-bromides with PBr_3 following known procedures.[62] Reduction of the bromides to the hydrocarbons **2a** and **2b** was achieved photochemically by reaction with tri-*n*-butyltin deuteride and hydride, respectively.[30] The isomeric purity of the products was better than 80%. The synthesis of **3** followed the literature procedure;[63] the syntheses of the adamantane derivatives **4** ($R = CH_3$, C_2H_5, n-C_3H_7 and C_6H_5) started with adamantanone which was reacted with the corresponding alkyllithium reagents or phenylmagnesium bromide, respectively, as described.[64] The corresponding bromides were derived from the alcohols by reaction with PBr_3 and reduced without purification (to avoid elimination reactions in the case of the alkyl derivatives) using tri-*n*-butyltin deuteride.

Spectra

^{13}C Fourier transform NMR spectra were measured in $CDCl_3$ solution [concentrations (M): **1a** 1.3, **1b** 0.8, **1c** 1.6, **1d** 0.6, **2a** 0.4, **2b** 0.7 and 0.5 for all adamantanes **4**] at 100.61 MHz (Bruker WH 400 spectrometer equipped with ASPECT 2000) and *ca.* 25 °C. The digital resolution is given in the tables. Resolution enhancement was used for the determination of the line splittings. Signal assignments were available from the literature for **1**,[65] **3**,[66] **4**, $R = CH_3$,[66] **4**, $R = C_2H_5$, n-C_3H_7,[67] and **4**, $R = C_6H_5$ [66]. For the isotopomers **2a** and **2b** the following $\delta(^{13}C)$ values (in ppm relative to TMS, experimental error ±0.01) were found: C-1 45.54/45.52; C-2 53.28/53.23; C-3 37.79/37.81; C-4 48.89/48.85; C-5 26.26/26.24; C-6 35.24/35.20; C-7 44.86/44.85; C-8 21.57/21.62; C-9 31.29/31.36; C-10 27.00/26.95; an unequivocal assignment of C-2, C-6, C-7, C-8, C-9 and C-1 was possible on the basis of the observed $J(^{13}C, ^2H)$ splittings by the following argument: C-2 is distinguished by the ^1J value; the other carbons all have vicinal interactions and show observable splittings only if the dihedral angle ϕ is between 0° and 60° or between 140° and 160°. The higher shielding of C-9 relative to C-10 agrees with earlier observations on related systems.[68] Of the remaining resonances, that of C-4 was distinguished from that of C-5 via a DEPT subspectrum[69] for CH groups; C-1 and C-3 were assigned through a 2D ^{13}C, ^1H shift correlation[70] based on $^3J(^{13}C, ^1H) = 7$ Hz, which showed the expected H-4/C-1 cross-peak. ^{13}C NMR isotope shifts for **2a** and **2b** will be reported separately.

For the isotope effect measurements (Table 4) a 1:1 mixture of the ^2H and ^1H compound with 17% (v/v) acetone-d_6 was used. The data reported by Everett[42] were obtained for neat samples.

Effects of ^2H quadrupolar moment

Line broadening of signals from spin-$\frac{1}{2}$ nuclei due to quadrupolar relaxation of neighbouring spin $I > \frac{1}{2}$ nuclei in the case of spin–spin coupling has been treated by Pople[38] for spin-1 nuclei. Such effects can lead to systematic errors in the determination of coupling constants.[40] The shape of the spin-$\frac{1}{2}$ nucleus spectrum depends under these circumstances on the dimensionless parameter $\eta = 10\pi T_1 J$, where T_1 is the spin–lattice relaxation time of the spin-1 nucleus and J is the scalar

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* Some authors prefer to use a $\cos^2 \phi$ term instead of $\cos 2\phi$; the original equation has been rearranged using $\cos^2 \phi = (\cos 2\phi + 1)/2$.

spin–spin coupling. If T_1 is known, it is possible to extract the correct J value from a line shape analysis of the spin-$\frac{1}{2}$ multiplet. For this purpose deuterium T_1 values for **1a–d** were determined by the inversion–recovery technique[39] on a Bruker WH 200 spectrometer (**1a** 1.66 s, **1b** 1.62 s, **1c** 1.58 s, **1d** 1.69 s). In order to correct the measured line splittings $\Delta\nu$, the dependence of the ratio $\Delta\nu/J$ on η was determined from a number of calculated spectra. Here, the $\Delta\nu$ values were extracted from the calculated curves using a curve-fitting procedure for overlapping Lorentzian lines.[71] As Fig. 5 shows, for $\eta = 20$ the error in J is 4%. For $T_1 = 1.6$ s as determined above, $J = 0.40$ Hz and $\Delta\nu = 0.38$. The limit is given by $\eta = 5$, which yields $J = 0.1$ and $\Delta\nu = 0.07$ for $T_1 = 1.6$ s. On this basis, empirical corrections for the coupling constants 2, 7_s and 4, 2_{ex} (Tables 1 and 2) were derived in an iterative way from Fig. 5 starting with a $\Delta\nu$ value obtained from a curve-fitting procedure for the experimental multiplet.

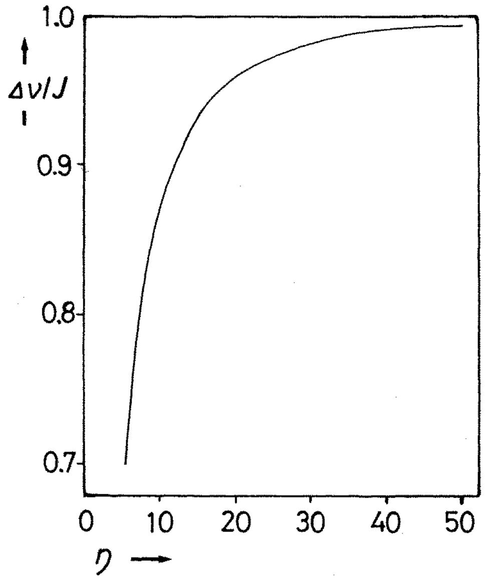

Figure 5. Plot of the ratio $J/\Delta\nu$ (see text) against the parameter η[38] that characterizes the line shape of multiplets of spin-$\frac{1}{2}$ nuclei coupled to spin-1 nuclei.

In addition to the work cited in Ref. 47, a number of calculated structures are available for **1**: *ab initio*,[72,73] MM2[74] and MNDO.[74] The present force field calculations were performed with the MMPI program package from Serena Software (Bloomington, IN, USA), based on QCPE program No. 395. For the FP–INDO calculations we used QCPE program No. 142, and the non-linear fitting procedure for the Karplus curves was carried out with the program NL-REGR,[75] rewritten in Pascal and adapted for the Bruker ASPECT 2000 computer.[76]

Note

A contribution by van Beuzekam *et al.*[77] which appeared after submission of this paper gives a detailed theoretical analysis of the α-substituent effect on $^3J(^{13}C, {}^1H)$ in the X—^{13}C—C—C—^{1}H fragment. In accordance with our experimental findings, this effect is small or even negligible for $X = CH_3$.

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