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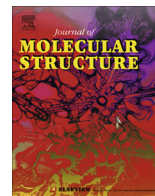**143** PUBLICATIONS **1,252** CITATIONS

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^{13}C NMR: $^{n}J_{CH}$ and $^{1}J_{CC}$ scalar spin–spin coupling constants (SSCCs) for some 3-monosubstituted 2-methylpropenes

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HIGHLIGHTS

- Experimental data for $^{n}J_{CH}$ and $^{1}J_{CC}$ SSCS for a series of methallylic derivatives.
- Geometries were calculated at the MP2/aug-cc-pVTZ level of theory.
- Theoretical calculations of the coupling constants with SOPPA (CCSD).
- The substituent effect was analyzed using empirical substituent parameters.

GRAPHICAL ABSTRACT

X = H, Cl, Br, I, OH, OMe, OEt, SH, SMe, SEt, NMe₂ and NEt₂.
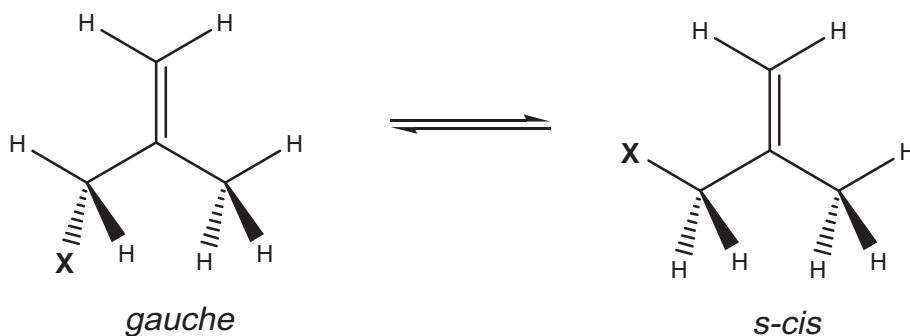
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ABSTRACT

Twelve methallylic derivatives were studied using ^{13}C NMR spectroscopy and theoretical calculations. Theoretical coupling constants were obtained with SOPPA (CCSD). All atoms were described by the EPR-III basis set, except for halogens, which were represented by the cc-pVTZ basis set. Geometries were optimized at the MP2/aug-cc-pVTZ level of theory, confirming previous results that the gauche and s-cis conformers predominate. Experimental $^{n}J_{CH}$ coupling constants were determined from coupled ^{13}C NMR spectra, while the $^{1}J_{CC}$ couplings were measured through the INADEQUATE technique. The experimental and theoretical values were in good agreement. Correlations with the usual substituent physicochemical parameters indicated that the $^{1}J_{C_3H_c}$ values (where Hc is attached to the C3 carbon bearing the substituent) exhibit good correlations with Taft's sigma (σ_I inductive parameter) and the Swain–Lupton Field Effect (F) ($R \sim 0.957$), while other correlations were not similarly significant (R values <0.9).

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1 Deceased.

Introduction

The allyl group is chemically significant because it is a building block for larger molecules, as recently described in a Claisen

rearrangement [1], in olefin metathesis [2] and in the synthesis of indoleketones [3]. This group is also of biological interest because it is observed in certain natural products, such as in garlic [4].

Thus, spectral analyses of allylic or methallylic compounds are informative for the analysis of complex spectral data from larger molecules.

The conformations of several allyl derivatives have been investigated through vibrational spectroscopy and theoretical calculations [5–8]. However, little study has been devoted to the corresponding methallyl derivatives. Most recent papers on the compounds studied in this work are from our laboratory, describing the conformational behavior of these compounds and the effects of substituents on some of their structural parameters using theoretical calculations, photoelectron spectroscopy, and also ^1H and ^{13}C NMR spectroscopies [9–12]. More recently [13], a comprehensive study on the conformational preferences of these compounds was also published using theoretical calculations and infrared spectroscopy. Some derivatives exhibited two or more conformers in CCl_4 solutions, with the *gauche* and *s-cis* conformers predominating. Theoretical calculations showed that depending on the substituent, up to six conformers were present (*gauche/-skew, gauche/skew, gauche/trans, s-cis/skew, s-cis/trans* and *s-cis/cis*), with some present in negligible amounts. Good agreement was observed between the experimental data and theoretical calculations.

Thus, the main objective of this work is to extend our previous structural studies of 3-monosubstituted 2-methylpropenes (methallylic derivatives) [$H_2C=C(CH_3)CH_2X$, X = Cl, Br, I, OH, OMe, OEt, SH, SMe, SEt, NMe_2 and NEt_2] by determining the $^nJ_{CH}$ and $^1J_{CC}$ scalar coupling constants from very complex NMR spectra. These constants were also determined using theoretical calculations, which confirmed the experimental assignments. The classical substituent effects on these couplings were briefly discussed.

Experimental and computational details

Compounds

Commercial 2-methylpropen-1-ol and 3-chloro-2-methylpropene were used without further purification. The bromo, iodo, methoxy, ethoxy, mercapto, methylthio, ethylthio, dimethylamine and diethylamine methallyl derivatives were prepared as previously described [9].

NMR experiments

For the $^nJ_{CH}$ measurements, the coupled ^{13}C NMR spectra were collected on a Varian Gemini 2000 300 spectrometer operating at 300.06 MHz for the ^1H frequency and at 75.45 MHz for the ^{13}C frequency. The spectra were obtained at 25 °C in 5 mm NMR tubes with samples prepared from 50% of compound in CCl_4 (v/v) with 5% cyclohexane-d_{12} for locking. The typical conditions were 2 s delay time, a spectral width of 12,300 Hz with 64 k data points and a line broadening (lb) of 0.1 Hz. For the J_{CC} measurements, the experiments were performed on a Bruker AM 500 spectrometer operating at 125.76 MHz when observing ^{13}C signals. Such spectra were recorded using 5 mm sample tubes from $CDCl_3$ solutions at 30 °C at concentrations of *ca.* 80% w/w. $^1J_{13C13C}$ coupling constants were measured at natural abundance using the INADEQUATE technique [14], which was adjusted for $^1J_{13C13C}$ = 60 Hz. ^{13}C signals were first assigned from the ^1H-coupled ^{13}C spectra and then confirmed when performing the INADEQUATE experiments. According to the acquisition parameters used here, the digital resolution was in the range of 0.07–0.21 Hz per point. All spectra were recorded at

the LANAIS NMR-500 facility of the Department of Physics, FCEyN, University of Buenos Aires.

Computational details

The most stable geometries were optimized as isolated molecules at the MP2/aug-cc-pVtZ level using the Gaussian03 package of programs [15]. All structures were verified as the minima on the potential energy surface by calculating the Hessian matrices. The spin–spin coupling constants were calculated using the Dalton11 program at SOPPA (CCSD) [16]. All atoms were described by the EPR-III basis set except for halogens, which were represented by the cc-pVTZ basis set. Calculations were carried out for the most stable conformer of each methallylic derivative, as in most cases these conformers accounted for more than 90% [13].

Results and discussion

One-bond carbon–proton coupling constants ($^1J_{CH}$)

Table 1 presents experimental $^1J_{CH}$ values for the four structural carbon atoms and also for those of the X-alkyl fragment. Note that the only couplings to exhibit significant changes upon the introduction of the substituent are $^1J_{C_3H_c}$ and $^1J_{C_5H}$, due to the direct attachment of the substituent (Scheme 1). Comparison of these values with $^1J_{C_3H_c}$ for 2-methylpropene [17] (the unsubstituted compound) allows the magnitude of these changes to be observed. These changes result from the substituent's effect on the effective nuclear charge of this carbon atom and were analyzed using empirical parameters related to the substituent (Table 2). The changes did not exhibit a good correlation with group electronegativity values [18,19], but reasonable correlations were found with Taft's inductive parameter (σ_I) [20] (r = 0.957) and with Swain and Lupton's field effect (**F**) [21] (r = 0.958) (Figs. 1 and 2, respectively). However, other effects may be at play including steric effects, which are strongly dependent on the heteroatom size and on orbital interactions (π_{cc}/σ_{cx}^*, σ_{cx}/π_{cc}^*, n_x/π_{cc}^* and $n_x/\sigma_{cc(x)}^*$), as was extensively discussed in a previous work [12].

The data in Table 1 also show that small changes in the $^1J_{C_1H_a}$ and $^1J_{C_1H_b}$ coupling constants are observed when different substituents are introduced at the C_3 position. In vinyllic systems, *trans* substitution is known to lead to a larger $^1J_{CH}$ than *cis* substitution [22]. In these methallylic derivatives, which have methyl substituents at the C_2 position, $^1J_{C_1H_a}$ and $^1J_{C_1H_b}$ couplings were assigned considering those changes in these coupling constants. This analysis accounts for the fact that the *gauche* conformers predominate [11], where this steric effect must make only a small contribution.

The $^1J_{C_4H_c}$ coupling constants of the methyl carbon (C_4) do not exhibit significant changes upon the introduction of different substituents at the C_3 position.
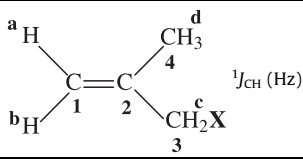
Table 1 also shows that R substituents presenting the same heteroatom do not result in noticeable changes in the $^1J_{CH}$ coupling constants for the C_3 and C_1 carbons.

In general, the experimental and theoretically calculated values for all $^1J_{CH}$ coupling constants are in reasonable agreement. The small deviations observed ($\leqslant 3$ Hz in ~140 Hz) only for $^1J_{C_3H_c}$ may be due to the fact that vibrational effects were not included in the calculations, since they require even longer computation times. For the remaining couplings the deviations are $\leqslant 1$ Hz.

Two-bond or geminal carbon–proton coupling constants ($^2J_{CH}$)

Two-bond carbon-proton coupling or *geminal* coupling ($^2J_{CH}$) can only occur for the C_2 carbon through π-bonding with vinyllic protons (H_a and H_b) and through σ-bonds with both methylene

Table 1

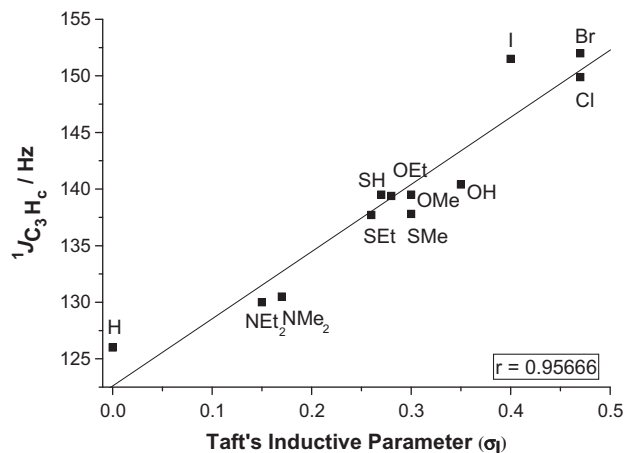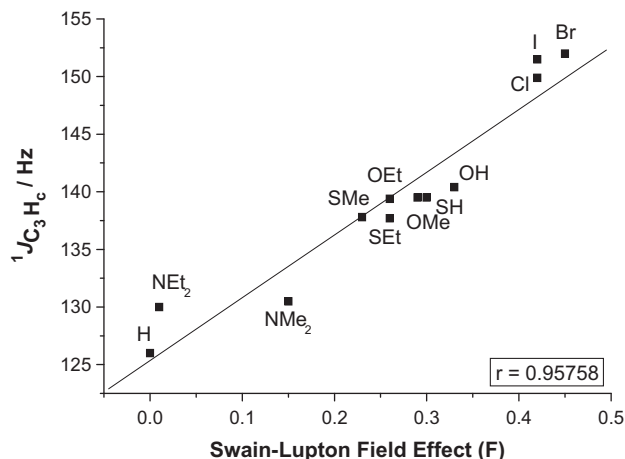Experimental and theoretically calculated[a] directly bonded ^{13}C, ^1H scalar coupling constants ($^1J_{CH}$) in Hz.

X	C_1H_a	C_1H_b	C_3H_c	C_4H_d	C_5[b]	C_6[b]
H	–(156.8)	–	126.0[c] (126.3)	126.0[c] (126.3)	–	–
Cl	157.0[d] (158.4)	–	149.9 (152.3)	126.8 (128.2)	–	–
Br	157.4 (159.9)	156.9 (157.9)	152.0 (152.1)	126.9 (129.6)	–	–
I	157.6 (160.3)	156.6 (158.1)	151.5 (152.4)	126.7 (128.3)	–	–
OH	156.4 (157.6)	155.5 (156.5)	140.4 (143.3)	126.0 (127.6)	–	–
OMe	156.3 (157.4)	155.4 (156.6)	139.5 (143.2)	126.1 (127.5)	140.1 (141.8)	–
OEt	156.4 (156.6)	155.4 (157.4)	139.4 (143.2)	126.1 (126.4)	139.9 (140.1)	125.8 (125.9)
SH	156.4 (158.9)	156.1 (156.6)	139.5 (141.9)	126.4 (127.8)	–	–
SMe	155.7[d] (158.1)	–	137.8 (140.6)	126.3 (127.7)	138.0 (140.3)	–
SEt	155.7[d] (156.9)	–	137.7 (140.8)	126.4 (127.7)	138.2 (141.7)	127.1 (127.6)
NMe_2	155.4 (156.8)	155.0 (156.7)	130.5 (132.7)	126.0 (127.5)	132.3 (133.8)	–
NEt_2	155.3 ([e])	154.7 ([e])	130.0 ([e])	125.9 ([e])	131.4 ([e])	125.0 ([e])

[a] Calculated values are given in parenthesis.
[b] C_5 and C_6 refer to the substituent alkyl group.
[c] From Ref. [17].
[d] Triplet for C_1H_a and C_1H_b couplings.
[e] These calculations did not reach completion.

X = H, Cl, Br, I, OH, OMe, OEt, SH, SMe, SEt, N(Me)_2 and N(Et)_2
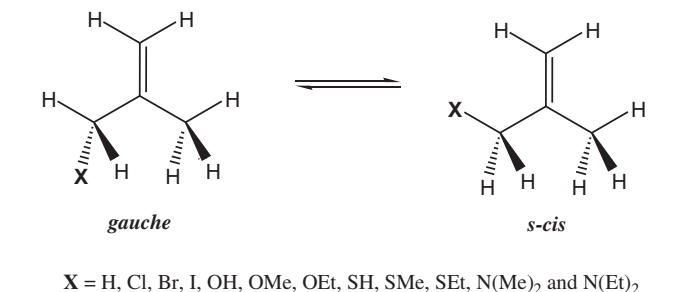
Scheme 1. Most stable conformers for some 3-monosubstituted 2-methylpropenes.

Table 2

Substituent group electronegativity (χ), [18,19] Taft's inductive parameter (σ_I) [20] and Swain–Lupton's field effect (**F**) [21].
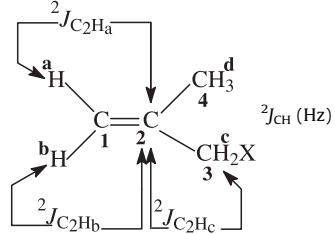
X	X	σ_I	F
H	2.176	0.00	0.00
Cl	3.16	0.47	0.42
Br	2.96	0.47	0.45
I	2.66	0.40	0.42
OH	3.494	0.35	0.33
OMe	3.543	0.30	0.29
OEt	3.544	0.28	0.26
SH	2.616	0.27	0.30
SMe	2.592	0.30	0.23
SEt	2.591	0.26	0.26
NMe_2	3.012	0.17	0.15
NEt_2	3.011	0.15	0.01

(H$_c$) and methyl (H$_d$) protons. The resonance of C$_2$ presents a very complex multiplet, mainly due to the small absolute values of *geminal* coupling constants. $^2J_{C_2H_a}$ and $^2J_{C_2H_b}$ coupling constants were assigned by comparison with data reported [23] for model compounds. The absolute values of $^2J_{C_2H_b}$ are greater than those of $^2J_{C_2H_a}$. In both cases, the magnitudes of the $^2J_{C_2H_a}$ and $^2J_{C_2H_b}$ couplings are small, resulting in small variations due to substituent effects (Table 3).

Fig. 1. Correlation between $^1J_{C_3H_c}$ and Taft's Inductive parameter (σ_I).

Fig. 2. Correlation between $^1J_{C_3H_c}$ and the Swain–Lupton Field Effect (**F**).

Table 3
Experimental and theoretically calculated[a] two-bond or *geminal* ^{13}C, ^1H coupling constants ($^2J_{CH}$) in Hz.

X	C_2H_a	C_2H_b	C_2H_c	C_2H_d
Cl	1.0 (0.1)	2.1 (−0.9)	4.3 (−4.1)	6.4 (−6.2)
Br	1.0 (0.2)	2.0 (−0.9)	3.7 (−2.9)	6.4 (−6.1)
I	1.0 (0.2)	1.9 (−1.0)	3.7 (−3.0)	6.4 (−6.1)
OH	1.4 (−0.6)	1.8 (−0.3)	4.3 (−2.0)	6.2 (−6.2)
OMe	1.4 (−0.4)	1.8 (−0.4)	4.1 (−2.0)	6.4 (−6.2)
OEt	1.3 (−0.4)	1.8 (−0.4)	4.1 (−2.0)	6.4 (−6.2)
SH	0.9 (−0.1)	1.6 (−0.6)	4.3 (−3.4)	6.3 (−6.1)
SMe	1.0 (−0.1)	1.8 (−0.5)	4.5 (−3.3)	6.3 (−6.1)
Set	1.1 (−0.1)	1.7 (−0.6)	4.6 (−3.3)	6.2 (−6.0)
NMe$_2$	1.6[b] (−0.2)	1.6[b] (−0.6)	4.8 (−4.0)	6.3 (−6.2)
NEt$_2$	1.5[b] ([c])	1.5[b] ([c])	4.8 ([c])	6.3 ([c])

[a] Calculated values are given in parenthesis.
[b] 2nd Order system.
[c] These calculations did not reach completion.

As expected, the coupling between the C_2 carbon and methyl protons (H_d) does not change with the introduction of different substituents (Table 3), while the coupling between the C_2 carbon and its methylene protons ($^2J_{C_2H_c}$) is considerably affected by the substituent type. In the $^2J_{C_2H_c}$ coupling system, the substituent localized at the C_β carbon (C_3) leads to positive contributions to the magnitude of $^2J_{C_2H_c}$ [24]. The extent of this effect depends on the electronegativity of substituent X. For propene, the signals of *geminal* coupling constants are assumed to be negative [22], an assumption that can be extended to all methallylic derivatives and confirmed by theoretical calculations. Comparing the $^2J_{C_2H_c}$ coupling constants to the $^2J_{C_2H_d}$ coupling constants (−6.2 to −6.4 Hz), which are free of substituent effects, all substituents make positive contributions to the $^2J_{C_2H_c}$ coupling constants. However, the $^2J_{C_2H_c}$ constant values do not exhibit linear correlations with the empirical electronegativity parameters of substituents (Table 2) [18,19] due to other effects.

Moreover, in the $^2J_{C_2H_c}$ coupling, the protons of allylic C—H bonds are placed α- to a $\pi C=C$ system and thus might exhibit orientation dependence. The corresponding carbonyl systems (^1H—$C_{\beta-}$—$^{13}C_\alpha=O$) [24,25] exhibited a maximum negative contribution to the coupling, as the H—C_β bond lies perpendicular to the carbonyl plane due to a $\sigma_{C_\beta-H}/\pi^*_{C_\beta=O}$ hyperconjugative interaction, which is more effective in the *s-cis* form. In methallylic derivatives, this effect may be small because the coupling constants represent the averaged values over different conformers, despite the fact that in methallylic derivatives the *gauche* conformer is predominant [11]. Thus, the observed variations in $^2J_{C_2H_c}$ coupling constants upon substitution can be due to competition among different effects. Here, it seems that the agreement between experimental and calculated values are not so good as for $^1J_{CH}$ because the figures are small, but in most cases the deviations are ⩽2 Hz, while for $^2J_{C_2H_d}$ are only ⩽0.3 Hz.

Three-bond or vicinal carbon–proton coupling constants ($^3J_{CH}$)

Different long range coupling pathways can be derived from the proton–coupling carbon NMR spectra of these compounds. Coupling through three bonds or *vicinal* coupling ($^3J_{CH}$) is observed

for C_1, C_3 and C_4 carbons, and three different coupling pathways can be considered. The C_3 and C_4 carbons couple with the H_a and H_b vinyllic protons through the $^{13}C—C=C—^1H$ fragment, and with the H_c methylene and H_d methyl protons through the $^{13}C—C(=C)—C—^1H$ system. The C_1 carbon couples with the H_c methylene and H_d methyl protons through the $^{13}C=C—C—^1H$ fragment. Experimental and theoretical $^3J_{CH}$ values are presented in Tables 4 and 5.
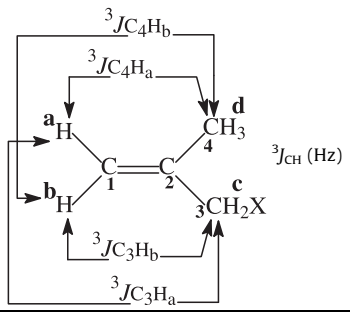
In the case of oxygen, sulfur and nitrogen methallylic derivatives, the resonance of the C_3 carbon is more complex due to the additional coupling between C_3 and the methylene or methyl protons of the substituent groups.

For the $^{13}C—C=C—^1H$ system, the heteronuclear ^1H, ^{13}C *trans* coupling constant is generally larger than the *s-cis* coupling constant, as observed in equivalent ^1H, ^1H systems [26]. In this case, the orientation of the π-bond does not influence the magnitude of the coupling because of the coplanarity of the whole system [27]. For methallylic derivatives, this occurs in the $^3J_{C_4H_a}$, $^3J_{C_4H_b}$, $^3J_{C_3H_a}$ and $^3J_{C_3H_b}$ coupling constants (Table 4). This table also shows that the substitution in the allylic fragments leads to significant changes in the magnitude of the $^3J_{C_3H_a}$ and $^3J_{C_3H_b}$ coupling constants, whereas the $^3J_{C_4H_a}$ and $^3J_{C_4H_b}$ coupling constants do not change considerably with the introduction of different substituents at the C_3 position. For the latter couplings, as the substituent is not directly bonded to either carbon involved in the coupling pathway, the small observed variations in the magnitude of the coupling constants could be due to through-space interactions between the substituents and the vinyllic group.

For the $^3J_{C_3H_a}$ and $^3J_{C_3H_b}$ couplings, the substituent is localized in the α-position related to the coupling pathway. Related studies [28,29] suggest that the complexity of this type of coupling is mainly due to the dihedral angle dependence between coupled atoms, to the substituent orientation in C_α (φ_α) and to the electronegativity (χ) of X. The extent of the electronegativity effect of X on coupled C_α depends on the angular orientation of X, and according

Table 4
Experimental and theoretically calculated[a] three-bond or *vicinal* ^{13}C, ^1H scalar coupling constants ($^3J_{CH}$) in Hz for the $^{13}C—C=C—^1H$ coupling system.
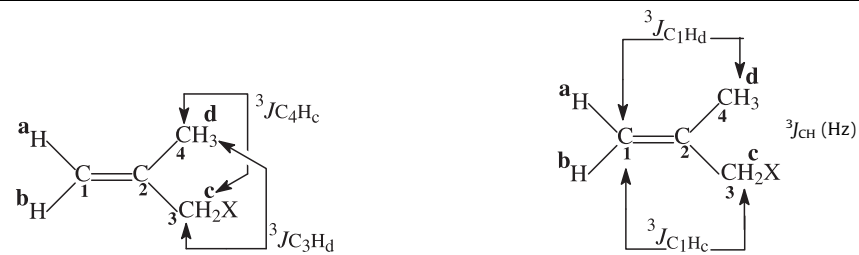
X	C_4H_a	C_4H_b	C_3H_a	C_3H_b
Cl	5.9 (5.1)[b]	10.4 (10.7)[b]	13.9 (15.0)[b]	7.6 (6.9)[b]
Br	5.8 (5.1)	10.3 (10.7)	14.4 (15.1)	7.7 (7.0)
I	5.8 (5.1)	10.3 (10.7)	14.5 (15.1)	7.8 (7.1)
OH	6.5 (5.1)[b]	11.1 (11.0)[b]	10.9 (12.9)[b]	6.6 (6.3)[b]
OMe	6.5 (5.4)	11.0 (11.2)	11.4 (12.9)	6.4 (6.1)
OEt	6.5 (5.4)	11.0 (11.2)	11.4 (12.9)	6.4 (6.1)
SH	6.0 (5.2)	10.7 (10.8)	12.9 (13.8)	7.2 (6.7)
SMe	6.1 (5.3)	10.7 (11.0)	12.4 (13.1)	6.8 (6.1)
SEt	6.3 (6.2)	10.4 (13.2)	11.9 (11.1)	7.2 (5.3)
NMe$_2$	6.3 (5.5)	10.9 (11.2)	11.4 (12.2)	6.4 (5.8)
NEt$_2$	6.3 ([c])	11.0 ([c])	11.3 ([c])	6.4 ([c])

[a] Calculated values are given in parenthesis.
[b] The experimental values from Ref. [26] are almost the same.
[c] These calculations did not reach completion.

Table 5
Experimental and theoretically calculated[a] three-bond or *vicinal* ^{13}C, ^{1}H scalar coupling constants ($^{3}J_{CH}$) in Hz for ^{13}C—$C(=C)$—C—^{1}H and $^{13}C=C$—C—^{1}H couplings systems.

X	C$_3$H$_d$	C$_4$H$_c$	C$_1$H$_c$	C$_1$H$_d$
Cl	4.4 (4.3)	3.7 (4.1)	5.2 (5.5)	5.7 (5.8)
Br	4.4 (4.6)	4.1 (4.3)	5.6 (5.8)	5.6 (5.9)
I	4.6 (4.9)	4.4 (4.9)	5.7 (6.0)	5.7 (5.9)
OH	4.3 (3.6)	2.6 (4.0)	4.7 (5.3)	5,8 (5.9)
OMe	3.9 (3.5)	3.0 (3.8)	4.7 (5.1)	5.8 (6.0)
OEt	4.0 (3.4)	3.0 (3.8)	4.7 (5.0)	5.8 (6.0)
SH	4.3 (4.3)	3.7 (4.1)	5.3 (5.6)	5.7 (5.9)
SMe	4.2 (4.3)	3.9 (4.1)	5.5 (5.7)	5.5 (5.9)
SEt	4.0 (4.1)	4.0 (4.3)	5.6 (5.7)	5.6 (5.9)
NMe$_2$	3.6 (3.6)	3.4 (3.4)	5.0 (5.1)	5.8 (9.0)
NEt$_2$	3.6 ([b])	3.2 ([b])	4.8 ([b])	5.7 ([b])

[a] Calculated values are given in parenthesis.
[b] These calculations did not reach completion.

to the torsional angle (φ_α, X—C$_\alpha$—C=C), this effect could lead to negative or positive contributions.

For $^{3}J_{C_3H_b}$ coupling, the dihedral angle [H—C=C—C(X)] between coupled atoms is approximately 0° and for $^{3}J_{C_3H_a}$ it is approximately 180°, and for both couplings, these angles do not vary with the type of substitution. Therefore, the variations observed for these couplings among substituents are mainly due to the angular dependence of X (φ_α) and to the electronegativity of X, with the latter dependent on the former, that is, the relative orientation of the substituent. Other factors such as through-space interactions between substituents and the vinyl group may also contribute to the magnitude of the $^{3}J_{C_3H_a}$ and $^{3}J_{C_3H_b}$ couplings.

In the ^{13}C—$C(=C)$—C—^{1}H system (Table 5), which includes $^{3}J_{C_3H_d}$ and $^{3}J_{C_4H_c}$ couplings, the vinyllic carbon is localized at the β-position related to the coupling pathway. In this case, the π electrons may participate in the coupling transmission as a result of hyperconjugative interactions between the π and σ orbitals of the allylic bonds. However, experimental studies [24] involving rigid systems such as *t*-Bu-cyclohexane derivatives found that the magnitude of couplings through the ^{13}C—$C(=C)$—C—^{1}H fragments are practically the same for protons in axial or equatorial positions and that those orbital interactions may be irrelevant.

The data presented in Table 5 show that substituents with different heteroatoms exhibit small variations in $^{3}J_{C_3H_d}$ and $^{3}J_{C_4H_c}$ couplings. In the $^{3}J_{C_4H_c}$ coupling, the substituent is localized at the γ-position relative to the coupling pathway, and γ-substituents are known to lead to negative contributions over $^{3}J_{CH}$ as the electronegativity of X is increased [28,30]. Although a rough correlation between $^{3}J_{C4Hc}$ and the substituent group electronegativity (χ) is observed ($r = 0.82767$), the changes in J values seem to be highly dependent on the geometric arrangements of the coupled atoms.

Moreover, for the $^{3}J_{C_1H_c}$ and $^{3}J_{C_1H_d}$ couplings in the $^{13}C=C$—C—^{1}H system, the π-bond orientation is an essential factor that must be considered [27]. Theoretical and experimental studies [27,30–32] have proposed a breakdown of the Karplus relationship for this heteronuclear system. Taking into account the presence of two independent transmission mechanisms and considering that the dihedral angle defined by the geometry of the bonds involved determines which of the two mechanisms dominates, these mechanisms must discussed. If Φ [H—C=C—C(X)] is ≈0 or 180° then the σ-electron mechanism predominates, operating as in analogous saturated systems with maximum contributions at approximately 5–7 Hz. On the other hand, when $\Phi \approx 90°$, the π-electron mechanism predominates due to π orbital interactions between the double bond and the σ orbital of the allylic C—H bond, with maximum contributions at approximately 5 Hz for couplings free of substituent effects. The effects of the nature, position and orientation of substituents present along the coupling pathway in $^{13}C=C$—C—^{1}H systems must also be considered as analogous to saturated systems.

The data presented in Table 5 suggest that there are no considerable variations in the $^{3}J_{C_1H_d}$ coupling constants among the different substituents. This finding is expected because the substituent is not directly bonded to either one of the carbons involved in the coupling pathway, whereas for $^{3}J_{C_1H_c}$, considerable variations in the magnitude of couplings can be observed among substituents with different heteroatoms. The $^{3}J_{C_1H_c}$ values decrease with increasing electronegativity of X. However, no linear correlation was observed between $^{3}J_{C_1H_c}$ and the electronegativity of X ($r = 0.85095$). This can be attributed to the influence of the dihedral angle between the coupled atoms, and also to the conformational equilibrium, which depends on rotamer populations.

A comparison of calculated with experimental values showed an excellent agreement (deviations of ⩽1 Hz), with a few exceptions they were <2 Hz (Table 4). For the data in Table 5 the agreement is even better (deviations ⩽0.5 Hz).

Directly bonded carbon–carbon coupling constants ($^{1}J_{CC}$)

Table 6 presents experimental and calculated $^{1}J_{CC}$ data obtained for some of the methallylic derivatives presented here. These data demonstrate that the $^{1}J_{C_2C_2}$ coupling constants do not change considerably as different substituents are introduced at the C$_3$ position, whereas the substitution in the allylic (C$_3$) fragment leads to significant changes in the magnitude of the $^{1}J_{C_2C_3}$ and $^{1}J_{C_2C_4}$ coupling constants when compared to the corresponding coupling constant (41.8 Hz) [33] for unsubstituted 2-methylpropene. However, no linear correlation was observed between these coupling constants and the empirical parameters listed in Table 2. Thus, the observed changes result from different effects.

Table 6
Experimental and theoretically calculated[a] directly bonded ^{13}C, ^{13}C scalar coupling constants ($^1J_{CC}$) in Hz.

$^1J_{CC}$ (Hz)			
X	C_1C_2	C_2C_3	C_2C_4
H[b]	72.6 (72.3)	41.8 (42.3)	41.8 (42.2)
Cl	72.8 (72.2)	44.1 (45.5)	43.6 (44.6)
Br	72.3 (72.3)	−[c]	43.9 (44.8)
I	−[c] (72.4)	−[c] (44.5)	−[c] (45.1)
OH	72.9 (70.1)	44.5 (44.7)	42.5 (42.7)
OMe	72.4 (70.7)	45.2 (44.8)	45.8 (42.6)
OEt	−[c] (70.9)	−[c] (44.9)	−[c] (42.6)
SH	72.9 (71.6)	42.6 (43.6)	43.4 (44.3)
SMe	−[c] (71.0)	−[c] (43.3)	−[c] (44.0)
SEt	72.2 (71.2)	42.6 (44.0)	43.2 (44.0)
NMe$_2$	72.4 (71.7)	44.9 (45.5)	42.7 (42.7)
NEt$_2$	72.4 ([d])	45.3 ([d])	42.7 ([d])

[a] Calculated values are given in parenthesis.
[b] From Ref. [33].
[c] Not determined.
[d] These calculations did not reach completion.

In general, a substituent placed α to a C—C bond leads to a linear increase in $^1J_{CC}$ with increasing electronegativity. However, various factors are known to determine the magnitude of $^1J_{CC}$, such as the hybridization of the interacting atoms, the electronic influence of substituents, steric and solvation effects, and the influence of the unshared pairs of heteroatoms [34]. This lone pair orientation effect of an atom placed α to the corresponding C—C bond is one of the most important stereospecific effects on $^1J_{CC}$ coupling that makes it so useful for studying conformation [25].

A comparison of calculated with experimental values showed an excellent agreement (deviations of ⩽1 Hz), with a few exceptions they were <3 Hz (Table 6).

Concluding remarks

All experimental coupling constants obtained from very complex spectra are in full agreement with the theoretically calculated values (deviations ⩽1 Hz), except for $^2J_{C_2H}{}^2J_{C2H}$ (Table 3). As the experimental values were carefully assigned, the small deviations (<2 Hz) in the later couplings can be attributed mostly to errors in the theoretical values or to second order effects, as the digital resolution was high enough to enable such measurements. It has to be taken into account that vibrational effects were not included in the calculations, since they require even longer computation times.

In general, changes in J_{CH} and J_{CC} values with the substituent are largely dependent on the electronegativity of the substituent, but other effects must also be considered, such as steric and solvation effects, the influence of lone pairs and several orbital interactions (π_{cc}/σ^*_{cx}, σ_{cx}/π^*_{cc}, n_x/π^*_{cc} and $n_x/\sigma^*_{cc(x)}$) [12].

Acknowledgments

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