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One-bond CC spin–spin coupling constants in silyl-substituted cyclopropenes

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Abstract

One-bond CC spin–spin coupling constants have been measured for three silyl-substituted cyclopropenes. Very small ${}^1J$(CC) values have been found for *endo*-cyclic single CC bonds, *i.e. ca.* 12 Hz for the alkyl substituted CC bond and < 3 Hz for that bearing a silyl substituent. A coupling of *ca.* 50 Hz has been observed for the double CC bond. The results are interpreted in terms of the s-electron distribution within the systems examined.

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1. Introduction

Cyclopropene and its derivatives are the subject of continuous interest; they are versatile intermediates in organic synthesis, and the electronic structure of these highly strained molecules is still intriguing and requires in-depth studies.

There is no doubt that one-bond CC spin–spin coupling constants can be a source of crucial information about the s-electron distribution within a given chemical bond [1]. Since the introduction of the INADEQUATE technique in 1980 [2] there has been a growing interest in this parameter. However, the main drawback of the method is its low sensitivity. The measurements can be performed at the natural abundance of ^{13}C provided that a large amount of the compound is available (*ca.* 200–300 mg) and the compound is stable enough to survive prolonged measurements. Cyclopropenes known hitherto fulfil neither of these requirements. Synthesis of these compounds is usually tedious, and in most cases their half-lives are short. Therefore, it is not surprising that the spectroscopic data which can be found in the literature for this group of the compounds are rather scarce. Only quite recently have ${}^1J$(CC) coupling measurements been performed for 2,3,3-triphenylcyclopropene-1-carboaldehyde [3].

Silyl-substituted cyclopropenes recently synthesized in our laboratory (see ref. 4 and the Experimental section) have turned out to be unusually stable. Furthermore, quite large quantities of these compounds could be obtained. This gave us an opportunity to measure a full set of one-bond CC spin–spin coupling constants for this group of compounds. In addition, the CH and CSi couplings have also been determined.

2. Results and discussion

The compounds studied are displayed in Fig. 1 where the system of labelling used for the carbon nuclei is also indicated.

The data obtained for cyclopropenes are listed in Tables 1 and 2. For comparison, the couplings for analogously substituted ethenes were also measured (Table 3).

In particular the couplings obtained for *cis*-$C_6H_{13}CH{=}CHSi(CH_3)_3$ (**4**) may serve as an excellent set of reference data: a value of ${}^1J$(CC) of 61.4 Hz was found across the double CC bond and one of 42.0 Hz across the single Csp^2Csp^3 bond. It is also relevant to recall that the substitution with a silyl group causes a considerable decrease in ${}^1J$(CC): by about 40 Hz for the CC coupling across a triple bond and about 10 Hz for that across a carbon–carbon double bond [1].

The ring closure exerts a considerable influence on all of the *J* values, but these changes are not equally

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TABLE 1. Chemical shifts $\delta(^{13}\mathrm{C})$ and $\delta(^{29}\mathrm{Si})$ in silyl substituted cyclopropenes **1–3**; all values are in ppm relative to TMS

Compound	δ(C1)	δ(C2)	δ(C3)	δ(C4)	δ(Si)
1	102.86	136.90	8.48	14.17	n.m.
2	102.15	136.25	8.18	28.90	−22.85
3	112.87	135.84	20.25	13.48	−10.89
	δ(C5) [a]	δ(C6) [a]	δ(C7) [a]	δ(C8) [a]	
	δ(C8) [b]	δ(C9) [b]	δ(C10) [b]	δ(C11) [b]	
1	135.15	136.18	128.63	130.32	
2 [c]	135.16	136.25	128.58	130.28	
3 [d]	145.60	129.39	128.22	127.31	

[a] Refers to compounds **1** and **2**. [b] Refers to compound **3**. [c] The remaining alkyl chain signals in **2**: 27.3, 32.1, 22.9 and 14.30. [d] The remaining signals in **3**: δ(C5) −0.89, δ(C6) 72.07; δ(C7) 86.64.

distributed. While the ^{1}J(CC) coupling across the double bond in the ring, 50.0 Hz in **1**, 49.9 Hz in **2**, and 49.0 Hz in **3**, is only moderately smaller, by *ca.* 12 Hz, than that in compound **4**, the couplings across the single bonds, C1C3 and C2C3, are greatly lowered. Thus, ^{1}J(CC) of 11.0 Hz (**1**), 11.8 Hz (**2**) and 12.8 Hz (**3**) has been found for the C2C3 bond bearing an alkyl substituent. In spite of many efforts, attempts to obtain a value of ^{1}J(CC) for the Cl–C3 bond (the one with a silyl substituent attached) were unsuccessful. However, it is well known that the INADEQUATE method is not very suitable for measurement of very small spin–spin couplings (see, for example, the very recent work of Bax *et al.*, [5]). In particular, the presence of the residual, central signal (the typical width in our experiments being 2–3 Hz) makes the observation of J(CC) smaller than 3 Hz very difficult. The smallest coupling constant which has been easily observed in our work is that across two bonds in **3**, $^{2}J(C1SiCH_3) = 5.4$ Hz (see Table 2). Therefore, failure to observe ^{1}J(C1C3) in any of the three compounds studied may indicate that it is much less than 5 Hz; this would be one of the weakest ^{1}J(CC) couplings yet found. Algebraically smaller (negative) ^{1}J(CC)'s have only been found for some derivatives of bicyclobutane, and those were measured with ^{13}C-labelled samples [6].

The couplings across the exocyclic CH, CC and CSi bonds are, on the other hand, substantially larger than the corresponding couplings in ethenes. In particular, the ^{1}J(C1Si) value of 89.5 Hz observed for compounds **1** and **2** falls in the region considered typical for acetylene derivatives. Thus, for example, a value of ^{1}J(CspSi) of 88.7 Hz was reported for $(CH_3)_3SiC\equiv CC_6H_{13}$ [7]; the corresponding value of ^{1}J(CSi) in *cis*-ethene **4** is only 66.3 Hz (Table 3). An exocyclic ^{1}J(C2C4) coupling of 54.9 to 55.8 Hz (**1–3**) is also considerably larger than the corresponding ^{1}J(CC) in **4** (42.0 Hz). The one-bond coupling between C3 and the attached proton, 167 Hz is larger than the one-bond Csp^{3}H coupling found in propene (125.6 Hz [8]), and is identical with the value of ^{1}J(CH) for unsubstituted cyclopropene [8]. The latter observation indicates that the influence of a silyl substituent is not transmitted to the distant atoms but it is limited to the adjacent carbons.

Ab initio calculations, those performed by Fronzoni and Galasso [10] for one-bond spin–spin couplings in unsubstituted cyclopropene using the *equation-of-motion* method, provided the following values, ^{1}J(CC) of 18.6 Hz across a single bond and ^{1}J(CC) of 67.60 Hz across a double bond. Taking into account the influence of a silyl substituent, which reduces the coupling by at least 10 Hz, there is quite a good agreement between Galasso's calculated values and our experimental results. Furthermore, Fronzoni and Galasso demonstrated that the couplings are dominated by the Fermi contact term. Orbital-dipole (OD) and spin-dipolar (SD) contributions, which are related to the

TABLE 2. Spin–spin coupling constants, J in Hz, in silyl substituted cyclopropenes

Compound	^{1}J(C1C2)	^{1}J(C2C3)	^{1}J(C1C3)	^{1}J(C2C4)	^{1}J(C1Si)	^{1}J(C3H3)
1	50.0	11.0	< 3	54.9	89.5	167.0
2	49.9	11.8	< 3	55.0	89.6	167.0
3	49.0	12.8	< 3	55.8	78.0	n.m.
	^{1}J(C5C6) [a]	^{1}J(C6C7) [a]	^{1}J(C7C8) [a]	^{1}J(C5Si) [a]	^{3}J(C5C8) [a]	^{3}J(C6C9) [a]
	^{1}J(C8C9) [b]	^{1}J(C9C10) [b]	^{1}J(C10C11) [b]	^{1}J(C5Si) [b]	^{3}J(C8C11) [b]	^{3}J(C9C12) [b]
1	48.8	54.8	55.4	73.8	8.9	11.2
2	48.6	55.0	55.4	73.8	8.9	11.2
3 [c]	59.1	56.2	55.6	54.0	8.6	9.0
	^{3}J(C1H4)	^{3}J(C3H4)	^{2}J(C2H3)	^{1}J(C4H4)		
1	5.3	3.3	< 0.5 [d]	129.0		
2	4.8	2.7				

[a] Refers to compounds **1** and **2**. [b] Refers to compound **3**. [c] The remaining J values in **3**: ^{1}J(C3C6) 51.5, ^{1}J(C7C8) 48.2, ^{2}J(C1SiC5) 5.4. [d] Confirmed by J-resolved experiment.

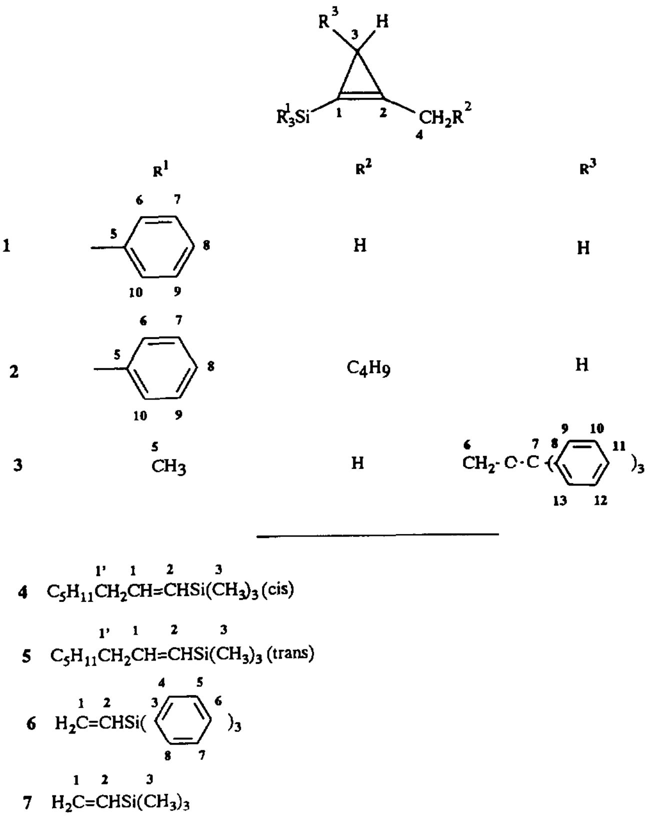
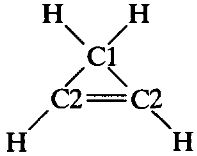


Fig. 1.

density of p-electrons, seem to play a minor role. This is a significant observation since it allows us to interpret the experimental ^1J values obtained in our work in terms of changes in the s-character of the carbon orbitals involved and to apply the known relationships which relate ^1J(CC) and ^1J(CH) values to the s-characters of relevant orbitals [1,8,11]. The emerging qualitative picture is quite clear. Thus, the small ^1J(C1C3) and ^1J(C2C3) coupling constants indicate that there is a large contribution of p-electrons to the C1C3 and C2C3 bonds. The large couplings across exocyclic C1Si, C3H, and C2C4 bonds, on the other hand, should be interpreted as favouring a large contribution of s-electrons to these bonds. Our conclusions are in agreement with the theoretical results of Eckert-Maksic and Maksic [12], who calculated the following hybridization indices for unsubstituted cyclopropene:



C1–C2 (3.68–2.65), C2=C2 (1.88–1.88), C1–H (2.49) and C2–H (1.64).

3. Experimental section

1-(Triphenylsilyl)-2-methylcyclopropene (**1**) and 1-(triphenylsilyl)-2-n-pentylcyclopropene (**2**) were synthesized as described previously [4] and compound **3** was made as follows: 1-(Trimethylsilyl)-2-methyl-3-(triphenylmethoxymethyl)cyclopropene (**3**) was obtained in three steps from *O*-(triphenylmethyl)-3-(trimethylsilyl)-2-propyn-1-ol: IR (film) 1810 cm^{-1}; MS (70 eV) *m/Z* 398 (M^+), 368, 243 (100%), 165, 155, 125 and 73; HRMS. Calcd. for $C_{27}H_{30}SiO$: 398.2066. Found: 398.2065; ^{1}H NMR (in dioxane-d_8, all values in ppm against TMS) $\delta = 0.14$ (s, 9H, TMS), 1.59 (q, 1H, CH_x (in ring), $^3J_{ax} = 5.7$ Hz, $^3J_{bx} = 4.3$ Hz), 2.18 (s, 3H, CH_3), 2.71 (q, 1H, CH_a0, $^3J_{ax} = 4.3$ Hz, $^2J_{ab} = 9.2$ Hz), 3.02 (q, 1H, CH_b0, $^3J_{bx} = 5.7$ Hz), 7.10–7.60 (m, 15H, aromat.).

The NMR spectra were recorded for samples in standard 5 mm tubes; a typical sample consisted of *ca.* 200 mg of a compound and 0.5 ml of dioxane-d_8 as a solvent. The measurements were carried out on a Bruker AM 500 spectrometer and the standard Bruker microprogram (32-phase Freeman cycle with automatic data storage was used in order to record the ^{13}C 1D INADEQUATE spectra.

The ^{13}C NMR spectra were recorded in both proton-decoupled and proton-coupled modes. A selective proton decoupling was performed in order to confirm the *J*(CH) values determined from the fully proton-

TABLE 3. Chemical shift (δ, ppm) and coupling constant (*J*, Hz) data for silyl substituted ethenes

Compound	$\delta(^{13}$C1)	$\delta(^{13}$C2)	$\delta(^{13}$C1′)	^1J(C1C2)	^1J(C1C1′)	^1J(C2Si)	^1J(C3Si)
4 [a]	149.07	128.60	33.61	61.4	42.0	66.3	51.7
5 [a]	147.97	130.87	37.77	60.6	40.2	67.5	52.0
6 [c]	136.73	133.90	[b]	59.6	[b]	69.0	70.8
7				58.8 [d]	[b]	64.7 [e]	52.2 [e]

[a] The remaining $\delta(^{13}$C) signals in **4**: 31.89, 29.81, 29.11, 22.66, 14.00, 0.15 and in **5**: 32.78, 29.87, 29.73, 23.58, 14.84, −0.4. [b] Not relevant. [c] The remaining ^{13}C data for **6**: δ(C3) 134.13, δ(C4) 135.90, δ(C5) 127.85, δ(C6) 129.53; ^1J(C3C4) 49.2 Hz, ^1J(C4C5) 54.7 Hz, ^1J(C5C6) 55.6 Hz ^3J(C3C6) 9.0 Hz, ^3J(C4C7) 11.1 Hz. [d] Taken from ref. 1, p. 324. [e] Taken from ref. 9.

coupled spectrum. The typical conditions for standard proton-decoupled ^{13}C spectra, measured at 125.76 MHz, were as follows: acquisition time 1.70 s, digital resolution 0.6 Hz per point and number of transients 800. The proton-decoupled ^{29}Si spectra were measured at 99.36 MHz using broad-band probe; spectral width 4950.5 Hz, acquisition time 3.31 s, pulse width 18.0°, pulse delay 2 s, number of scans 256. The ^{13}C INADEQUATE spectra of compounds **1**–**3** were recorded three times for the following settings, $J = 5$ Hz, $J = 12.5$ Hz and $J = 50$ Hz. This corresponds to the delays 50 ms, 20 ms and 5 ms, respectively. For the compounds **4**–**6** the delay was set to 4.16 ms ($^1J(CC) = 60$ Hz). The typical acquisition time was of 1.70 s and this gave a digital resolution of *ca*. 0.6 Hz per point. The pulse delay was set to 2 s. The typical measuring time was 16 h.

The ^{13}C and ^{29}Si chemical shifts are reported relative to internal TMS. The ^1H and ^{13}C NMR spectra of compound **3**, which contains an $Si(CH_3)$ group, were determined relative to dioxane and then re-referenced to TMS. The ^{29}Si spectra were measured twice, without TMS and with TMS added.

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