

4. Long-Distance Effect on One-Bond C–C Scalar Couplings upon Introduction of a Double Bond in Bicyclic Systems

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Anomalous variations of one-bond C–C scalar coupling constants are observed in going from trinorbornane- to trinorbornene-like structures. Most notably, a 10-Hz increase is observed in the coupling constant involving the C-atoms of the ethano branch facing the C=C bond. An effect of about half the size is characteristic of higher homologues (bicyclo[2.2.2]octenes), but no such effect is observed for monocyclic molecules.

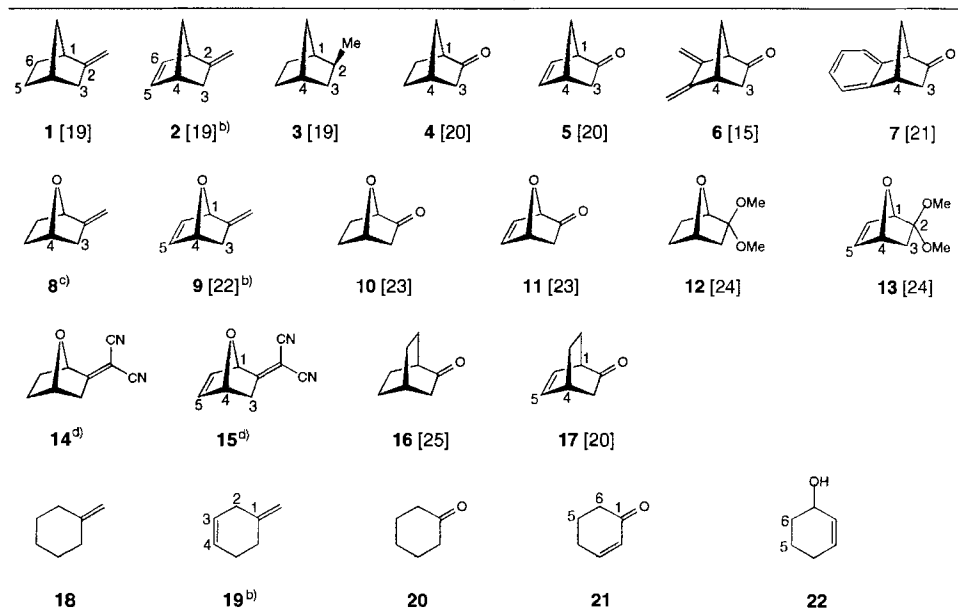
Introduction. – The C=C bond present in trinorbornene shows exceptional reactivity (see *e.g.* the *x*-factor [1]) and *exo*-face selectivity [2] [3]. These observations are probably consequences of its non-planarity [4] [5], which is confirmed by neutron diffraction [6]. Several theoretical studies have been performed to elucidate the nature of the anomalous geometry. Recent high-level calculations [7] were able to show the relevance of hyperconjugation, that is mixing effects between π electrons of the C=C bond and the σ bond of adjacent C–C bonds, in determining the structure of the C=C bond. However, the presence of steric hindrance in such strained system is able by itself to qualitatively reproduce the pyramidal arrangement of the protons of the C=C bond [8]. The associated structural and electronic rearrangement should not go undetected to NMR spectroscopy, due to the nature of the latter as local probe at the nuclear level. However, the only anomalies reported so far in the spectra of analogues of trinorbornene concern mainly the resonance of the methylene bridging group [9–16] or its substituents, which can be explained on the basis of the bicyclic structure and the proximity to the C=C bond.

In this report, we investigate the one-bond C–C scalar coupling constant ($^1J(\text{C},\text{C})$) in a series of bicyclic and monocyclic systems, since this parameter is known to be a sensitive probe of fine structural and electronic changes [17] [18].

Results. – We report in *Table 2* the values of the one-bond C–C scalar coupling constants for a series of mono- and bicyclic compounds (*Table 1*) either measured by us or taken from the literature. The molecules listed in *Table 1* consist mainly of pairs of substituted trinorbornanes and corresponding trinorbornenes, for the purpose of highlighting changes in the NMR parameters in going from one system to the other. Also, we investigated a few other bicyclic and monocyclic compounds in order to single out those effects that are characteristic of trinorbornene systems only.

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Table 1. Bicyclic and Monocyclic Compounds Analyzed in This Work^{a)}

^{a)} References provide synthetic method and/or NMR data. ^{b)} For convenience, the skeleton numbering is not systematic. ^{c)} Obtained by condensation of **10**, with (MePPh₃)Cl/NaNH₂/*t*-BuOK. ^{d)} Obtained by condensation of **10** or **11**, resp., with malononitrile/piperidine.

Table 2. ¹J(C,C) Coupling Constants of Compounds 1–22 (see Table 1)

	¹ J(C(a),C(b))/Hz								
	1, 2	2, 3	3, 4	4, 5	5, 6	6, 1	1, 7	4, 7	Others
1 ^{a)}	39.6	37.3	32.5	31.0	32.5	30.7	31.1	29.6	74.2
2 ^{a)} ^{b)}	36.1	47.3	31.1	42.6	67.3	40.0	31.0	30.4	75.4
3 ^{a)}	32.2	32.0	30.0	^{c)}	^{c)}	31.4	30.1	^{c)}	^{c)}
4	38.3	35.0	32.6	31.8	32.1	28.0	31.3	29.2	–
5	34.5	45.4	30.4	37.1	^{c)}	33.5	31.8	29.9	–
6	37.5	37.5	37.9	39.7	75.0	35.6	30.9	30.7	75.7, 85.7
7	34.7	41.8	30.9	40.9	^{c)}	37.8	29.8	^{c)}	^{c)}
8	42.9	40.6	34.7	^{c)}	^{c)}	33.1	–	–	75.5
9 ^{b)}	39.8	49.9	31.3	39.6	^{c)}	38.6	–	–	76.5
10	42.8	38.1	35.6	33.5	33.5	30.5	–	–	–
11	39.8	48.2	32.9	38.9	71.7	36.2	–	–	–
12	49.0	44.8	35.0	34.7	33.7	34.2	–	–	–
13	45.1	54.6	31.8	39.7	40.0	40.3	–	–	–
14	40.8	39.9	35.9	33.8	^{c)}	31.4	–	–	^{c)}
15	38.2	50.0	31.0	39.2	71.9	37.4	–	–	^{c)}
16	38.4	34.5	30.8	33.3	31.2	29.9	^{c)}	^{c)}	^{c)}
17	35.5	40.7	31.6	38.2	65.5	36.0	30.3	28.9	37.7
18 ^{a)}	39.7	31.9	33.3	33.3	31.9	39.7	–	–	72.3
19 ^{a)} ^{b)}	40.0	40.0	60.0	40.5	33.3	40.0	–	–	73.0
20	37.8	30.4	33.1	33.1	30.4	37.8	–	–	–
21	50.5	^{c)}	38.0	32.0	31.6	39.8	–	–	–
22	44.8	^{c)}	39.6	32.9	32.5	36.8	–	–	–

^{a)} Data from [19]. ^{b)} Atom numbering does not follow IUPAC rules, see text. ^{c)} Not determined due to signal overlapping.

A comparison of the results for compounds **1** and **2** (Table 2) exemplifies well the modification we observed in the scalar couplings relative to the ring skeleton upon introduction of a C=C bond at positions 5,6 in the trinorbornane structure. In the case of **1**, the measured $^1J(\text{C,C})$ s for the C-skeleton of the rings agree well with the linear correlation commonly found between value of the coupling constant and hybridization state of the C-partners [17], which is an indication that the *Fermi* contact term is the principal contribution to the scalar coupling. In line with this principle, the introduction of a C=C bond in a bicyclic structure such as in compound **2** causes a change in the bonds directly involved (between C(5) and C(6), C(1) and C(6), and C(4) and C(5)) so that bonds which contain sp^2 C-atoms show the largest couplings. Remarkably, in this latter compound, other effects are detectable in the remote part of the skeleton, not expected on the basis of the change of hybridization of the C-partners. The most striking effect is a 10-Hz increase of the one-bond C–C coupling constant of the ethano branch, which cannot be explained in terms of the simple correlation with the hybridization state since, formally at least, the C-atoms at positions 2 and 3 remains sp^2 and sp^3 , respectively, as in the parent compound **1**. In parallel, we observe a decrease of the coupling constants for the bonds involving one bridgehead C-atom and one C-atom of the ethano branch, that is bonds between C(1) and C(2) and between C(3) and C(4). The trend described here, that is an increase of ca. 10 Hz for the coupling constants relative to the ethano branch and a smaller decrease for those involving the neighboring bonds, is maintained if we replace the methyldene moiety in position 2 in **1** and **2** by a carbonyl group, as in ketones **4** and **5**. The data reported for 2-*exo*-methyltrinorbornane **3** [19] shows that the $^1J(\text{C,C})$ coupling constants of a trinorbornane system that does not have a sp^2 -hybridized C-atom are quite similar to those found for simpler alkanes [16] [17]. Remarkably, the introduction of two exocyclic C=C bonds in position 5 and 6 of compound **6** does not produce a coupling constant of the ethano branch any larger than observed for substituted trinorbornanes, even though the hybridization of the C-atoms of the skeleton of **6** is the same as in **5**. A smaller effect of ca. 4 Hz is observed when the electrons of the C=C bond are partially delocalized, as in the case of benzotrinorbornene **7**. Substitution of the bridging CH_2 by an ethereal bridge to produce 7-oxatrinorbornane(ene) derivatives does not produce any significant change in the described effect, as exemplified with data collected for compounds **8–15**. Higher homologues of trinorbornene, that is the substituted bicyclo[2.2.2]octene **17**, do show a variation of the $^1J(\text{C,C})$ s in the same direction as shown by tribornorbornenes, but of just about half the size of the effect. The measured $^1J(\text{C,C})$ coupling constants for cyclohexanes and cyclohexenes is in line with the hybridization state of the partner C-atoms (compounds **18–22**), and no other effects are detected elsewhere along the skeleton.

Discussion. – NMR has been used to investigate structural features of trinorbornane analogues, due to the interesting properties and peculiar geometry of this system. A series of NMR ‘effects’ has been described regarding the spectral differences between saturated and unsaturated compounds. Most notably, large chemical-shift variations have been observed upon introduction of a C=C bond for the C-atom of the methylene bridge of trinorbornene itself or for a series of analogous structures in which the bridging methylene group had been replaced by different heteroatoms (O [26], N [27], P [28], Si [29]). These effects can be understood, at least in a qualitative fashion, in terms of small

structural variations in going from the saturated compounds to the corresponding alkenes combined with the influence on the resonance of the bridging nuclei of the proximity of the C=C bond [28].

The effect we report here on the $^1J(\text{C},\text{C})$ coupling constants has its own peculiarities and resist to a straightforward interpretation in terms of simple, phenomenological theories. This is probably due to the (so far) elusive nature of the forces that determine the ground-state geometry and electronic distribution of trinorbornene-like structures. In fact, there has been discussion in the literature whether the characteristic tilting of the protons on the C=C bond in trinorbornene is mainly due to torsional constraints [8] or rather to interactions of π electrons of the C=C bond with the neighboring C–C σ bonds (hyperconjugation) [7] [30]. Steric effects have been shown to be able to account for some of the tilting, but quantitative agreement is achieved only after including mixing effects [7]. Hyperconjugation was also shown in another study to constitute the largest intramolecular interaction that contribute to the geometry of the C=C bond [30].

Much of the success in using $^1J(\text{C},\text{C})$ coupling constants is the useful linear correlation found in many organic molecules between this parameter and the hybridization state of the C-atoms participating in the bond [17]. *E.g.*, an interpretation of our results in terms of such a simple direct correlation would indicate that the C(2)–C(3) bond shows a certain amount of double-bond character and that the C(1)–C(2) and C(3)–C(4) bonds are somewhat weaker than a regular single bond, the signatures of a partial *retro-Diels-Alder* reaction. A test for this interpretation should be the comparison of the bond lengths in parent trinorbornane and trinorbornene. By electron diffraction, trinorbornane in the gas phase shows a longer C(5)–C(6) bond (1.573 Å) than the C(1)–C(6) bond (1.536 Å) [31]. A somewhat smaller bond-length differentiation is found by X-ray diffraction of crystalline trinorbornane (C(1)–C(6) 1.536 Å, C(5)–C(6) 1.546 Å) [32]. No accurate structural data are available for the parent trinorbornene. Neutron-diffraction measurements of bicyclo[2.2.1]hept-5-ene-2-*exo*,3-*exo*-dicarboxylic anhydride show a C(1)–C(2) of 1.572 Å and a C(2)–C(3) of 1.541 Å [6]. High-level quantum calculations predict for trinorbornene a C(1)–C(6) of 1.561 Å and a C(5)–C(6) of 1.555 Å [7]. This data suggests that the C(5)–C(6) bond is shortened when going from trinorbornane to trinorbornene, whereas the C(1)–C(6) bond is lengthened when going from trinorbornane to trinorbornene, in agreement with our ‘hyperconjugative’ model.



More experimental data are required to put this hypothesis on firmer ground. Our data are, nevertheless, an indication that upon introduction of a C=C bond in a trinorbornane-like system, a general rearrangement of the electron density might occur. To this respect, it is striking that we do observe a constant enhancement of *ca.* 10 Hz regardless of what is the nature of the substituent in position 2. On the other hand, the effect on the coupling constant concerning the ethano branch seems to be ‘tunable’, in the sense that it is proportional to the electron density on the C(5)–C(6) bond, as demonstrated in the case of compound 7. No influence is observed by replacing the methylene bridge by an

O-atom, which is in line with the known result that this molecular subunit plays a little role in determining the ground-state geometry of the C=C bond in trinorbornene [4]. We cannot exclude that all observed effects on scalar couplings may be due to the peculiar relative position of the bonds in the trinorbornene-like structures. This could affect the coupling constant also *via* contributions other than the usually dominant *Fermi* contact term, such as the spin-orbit or dipolar interaction.

Comparison of the $^1J(\text{C,C})$ values for the 3,4-bonds in **6** and **7** show a larger difference (7 Hz) than for the pairs of compounds **1, 2** (1.4 Hz) and **4, 5** (2.2 Hz). We have no explanation to offer at this moment for this phenomenon.

Conclusion. – We discovered a novel effect which consists in an unexpected variation of some $^1J(\text{C,C})$ coupling constants involving the skeleton bonds upon introduction of a C=C bond in a saturated trinorbornane-like system. We observe a large increase of the scalar coupling constant relative to the ethano branch, which is opposite to the C=C bond, with respect to the saturated compound. Also, a smaller variation and in the opposite direction is experienced by the adjacent bonds. The effect is present in all compounds investigated, which includes substituted trinorbornenes and 7-oxatrinorbornenes. Smaller effects in the same sense are observed for the higher homologues bicyclo[2.2.2]octanes. On the other hand, monocyclic hexanes do not show any unexpected alterations of the coupling-constant values upon introduction of an endocyclic C=C bond.

The spectra were recorded at the high-field NMR facility for the ‘Suisse Romande’. This work was partially supported by the *Swiss National Science Foundation* and the *Fonds Herbette* (Lausanne).

Experimental Part

General. See [33]. One-bond C–C scalar coupling constants were measured using the 1D version of the INADEQUATE technique [34] [35]. All samples were degassed by a few freeze-pump-thaw cycles and then sealed. The concentration of the samples was *ca.* 1M in CDCl_3 . All spectra were recorded on a *AMX2-600-Bruker* spectrometer at the frequency of 150.19 MHz, with a size of 128 K leading to a digital resolution between 0.2 and 0.4 Hz.

2-Methylidene-7-oxabicyclo[2.2.1]heptane (8). A soln. of 7-oxabicyclo[2.2.1]heptan-2-one (**10**) [23] (0.55 g, 5 mmol) in Et_2O (10 ml) was added to a suspension of instant ylid ((MePPh₃)Cl)/ NaNH_2 ; 3.39 g, 9 mmol) and *t*-BuOK (0.1 g) in Et_2O (20 ml) stirred at -78° under Ar. The mixture was allowed to warm up to 20° in *ca.* 1 h, and stirring was continued overnight. After addition of sat. aq. NH_4Cl soln. (20 ml), the mixture was extracted with CH_2Cl_2 (10 ml, 3 times), the combined extract dried (MgSO_4) and evaporated, and the residue purified by flash chromatography (silica gel, pentane/ Et_2O 1:1). Concentration was carried out by distillation of the solvents at atmospheric pressure. The residue was mixed with CDCl_3 (4 ml) and CH_2Cl_2 (10 ml) and the solvent distilled off until disappearance of the $^1\text{H-NMR}$ signal of CH_2Cl_2 . The CDCl_3 soln. of **8** so-obtained was used for the NMR analysis. $^1\text{H-NMR}$ (250 MHz, CDCl_3): 4.91, 4.74 (2 br. s, $\text{CH}_2=\text{C}(2)$); 4.71 (*d*, $^3J = 4.6$, H–C(1)); 4.64 (*t*, $^3J = 4.9$, H–C(4)); 2.42 (*dddd*, $^2J = 15.5$, $^3J = 4.8$, $^4J = 2.4$, 2,3, $\text{H}_{\text{exo}}\text{-C}(3)$); 2.10 (*dt*, $^2J = 15.5$, $^4J = 1.8$, $\text{H}_{\text{endo}}\text{-C}(3)$); 1.85–1.50 (*m*, $\text{CH}_2(5)$, $\text{CH}_2(6)$). $^{13}\text{C-NMR}$ (100.6 MHz, CDCl_3): 150.7 (*s*, C(2)); 102.4 (*t*, $^1J(\text{C,H}) = 157$, $\text{CH}=\text{C}(2)$); 80.4 (*d*, $^1J(\text{C,H}) = 153$, C(1)); 77.0 (*d*, $^1J(\text{C,H}) = 155$, C(4)); 38.8 (*t*, $^1J(\text{C,H}) = 132$, C(3)); 30.3 (*t*, $^1J(\text{C,H}) = 134$, C(5)); 29.2 (*t*, $^1J(\text{C,H}) = 135$, C(6)).

2-(7-Oxabicyclo[2.2.1]hept-2-ylidene)propanedinitrile (14). A mixture of **10** [23] (1.857 mg, 7.65 mmol), propanedinitrile (2.136 g, 32 mmol), and piperidine (50–200 mg) in MeOH (60 ml) was stirred at 60° for 3 h. Solvent evaporation and filtration on a short column of silica gel (CHCl_3 /light petroleum ether 5:2) gave 0.795 g (65%) of **14**. Colorless crystals. M.p. $55\text{--}56^\circ$. $^1\text{H-NMR}$ (250 MHz, CDCl_3): 5.31 (*d*, $^3J = 5.8$, H–C(1)); 4.91 (*t*, $^3J = 5.1$, H–C(4)); 2.86 (*dd*, $^2J = 19.2$, $^3J = 5.1$, $\text{H}_{\text{exo}}\text{-C}(3)$); 2.61 (*d*, $^2J = 19.2$, $\text{H}_{\text{endo}}\text{-C}(3)$); 2.18–1.55 (*m*, $\text{CH}_2(5)$, $\text{CH}_2(6)$). $^{13}\text{C-NMR}$ (100.6 MHz, CDCl_3): 185.0 (*s*, C(2)); 110.6, 110.0 (2*s*, 2 CN); 80.1 ($^1J(\text{C,H}) = 167$, C(1)); 78.5

(s, C(CN)₂); 76.9 (d, ¹J(C,H) = 163, C(4)); 41.7 (t, ¹J(C,H) = 138, C(3)); 27.8 (d, ¹J(C,H) = 140, C(5)); 27.6 (d, ¹J(C,H) = 135.8, C(6)). Anal. calc. for C₉H₈N₂O (160.18): C 67.49, H 5.03, N 17.49; found: C 67.57, H 4.99, N 17.59.

. 2-(7-Oxabicyclo[2.2.1]hept-5-en-2-ylidene)propanedinitrile (15). As described for 14, starting with 11 [23]: 85% of 15. Colorless crystals. M.p. 54°. ¹H-NMR (250 MHz, CDCl₃): 6.78 (dd, ³J = 5.7, 1.7, H-C(5)); 6.46 (dd, ³J = 5.7, 1.9, H-C(6)); 5.59 (m, H-C(1)); 5.35 (br. dd, J = 4.0, 1.7, H-C(4)); 2.86 (dd, ²J = 17.0, ³J = 4.0, H_{exo}-C(3)); 2.47 (d, ²J = 17.0, H_{endo}-C(3)). ¹³C-NMR (62.9 MHz, CDCl₃): 180.0 (s, C(2)); 141.7 (d, ¹J(C,H) = 181, C(5)); 130.4 (d, ¹J(C,H) = 184, C(6)); 111.3, 110.6 (2s, 2 CN); 81.4 (d, ¹J(C,H) = 154, C(1)); 78.9 (s, C(CN)₂); 77.5 (d, ¹J(C,H) = 146, C(4)); 37.0 (t, ¹J(C,H) = 139, C(3)). Anal. calc. for C₉H₆N₂O (158.16): C 67.35, H 3.82, N 17.71; found: C 68.47, H 3.88, N 17.61.

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