One-bond $^{13}$C-$^{13}$C coupling constants for the stereochemistry of hydrocarbons

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One-bond $^{13}$C-$^{13}$C coupling constant has played a very important role in elucidation of the carbon skeleton of organic molecules. Although its application has been very limited due to its low natural abundance, recent advances in high field NMR spurred even the use of 2D experiments to obtain the unambiguous structural information in samples with natural abundance. The one-bond $^{13}$C-$^{13}$C coupling constant not only gives direct information of connectivities of organic molecules but also becomes the source of the stereochemical information of organic molecules.

Kroivdin and his co-workers first reported that the difference in one-bond $^{13}$C-$^{13}$C coupling constants between anti- and syn-orientation carbon in oximes were larger than 7 Hz. We also previously reported that the coupling constant for anti position of an imine, which is syn to the nitrogen lone pair, was always about 10 Hz larger than that of syn carbon. Only a few stereospecificities of couplings are observed such as axial and equatorial bonds in $^{13}$C-1-methyl-1,4-di- methylcyclohexane and its trans isomer at about 180 Hz and series of mono- and di-substituted cyclopropanes, where greater coupling constants have been found in trans substituted compounds. These dependencies of coupling constants on configuration is generally considered that steric effect plays an important role. Although the electronegativity effect across the double bond showed that the coupling constant of cis-bond was ca. 3 Hz larger than that of trans-bond in 1-bromopropene, the stereochemical observation of steric effect in olefins by one-bond $^{13}$C-$^{13}$C coupling constant, however, has never been studied.

In the continued study on application of the coupling constants for the stereochernical analysis, we report here one-bond $^{13}$C-$^{13}$C coupling constants of the several cis and trans olefin compounds, and show the discrimination of stereoisomers of bicyclic compounds, in which there will be only the steric effect, by $^{13}$C-$^{13}$C one-bond coupling constants.

Experimental Section

NMR experiment All spectra were recorded using Bruker AMX-500 spectrometer. $^1$H (500.13 MHz) and $^{13}$C (125.76 MHz) spectra were obtained using 5 mm probe. 3 M solutions in CDCl$_3$ were used at ambient probe temperature of ca. 21-22 °C. The assignments of peaks were accomplished by the combined use of 1D and 2D-NMR techniques. 1D INADEQUATE pulse sequence, $90^\circ$ - τ - $180^\circ$ - τ - 90° - Δ - 90° provided by Bruker, was used to measure $^{13}$C-$^{13}$C cou-

Figure 1. The expanded partial 1D-INADEQUATE spectrum of (a) trans- and (b) cis-1-bromo-2-pentene (7). Bruker AMX-500 spectrometer, 3 M in CDCl$_3$, relaxation delay 3 s, 10240 scans. The data were acquired with 64 K data points multiplied by exponential (LS=-1.5).
pling constants. The value of $r$, which varied the amount of double quantum, was not optimized. Thus, the $r$ value used for all INADEQUATE experiments was 6.25 ms ($r = 40$ Hz). The 1D-INADEQUATE spectra were collected with 2-3 s relaxation delay and 64 K data point over a 4000 Hz to give ca. 0.06 Hz digital resolution. Data were processed using exponential multiplication with 1.5 Hz line broadening and 5 degree of polynomial baseline correction. Although the singlet of $^{13}$C peak did not completely disappear in the INADEQUATE spectrum, most of the one-bond $^{13}$C-$^{13}$C couplings were shown on the spectrum and the coupling constants were obtained directly from the spectra.

**Material.** All compounds were commercially available (Aldrich and Fluka) and used without further purification.

**Results and Discussion**

The representative $^{13}$C 1D-INADEQUATE spectrum of cis- and trans-1-bromo-2-pentene is shown in Figure 1. All the olefins studied were shown in Table 1 with their cis- and trans-bond $^{13}$C-$^{13}$C coupling constants, respectively. The differences of one-bond $^{13}$C coupling constant between trans- and cis-bonds of olefins studied are in the range of ca. 0.3-1.3 Hz. Thus, all the coupling constants of trans-bonds are larger than those of the corresponding cis-bonds. Although the difference of the coupling constant is not as large as that of the oximes and amides, the trend of the coupling constant is consistent with the steric effect to distinguish the two isomers of olefins studied.

While the electronegativity effect of substituent across the double bond showed that the coupling constant of cis-bond was ca. 3 Hz larger than that of trans-bond in 1-bromopropene, the observed coupling constant in this study, however, showed the coupling constant of trans-bond is larger than that of cis-bond. Therefore, the observed coupling constant differences in this study are mainly due to the steric effect. This small steric effect is consistent with the result of the axial bond and equatorial bond coupling constants in the 1,4-dimethylenecyclohexane, where the coupling constant of equatorial bond is ca. 0.8 Hz larger than that of axial bond. As can be seen in the compounds 5 and 7, the electronegativity effect on the difference of coupling constants between two isomers is negligible unless the substituents are attached to the double bond directly.

In order to check the applicability of this coupling constant trend, we studied several bicyclic compounds, 8, 9, and 10, which are of great interest for the NMR parameters and showed the coupling constants and their structures in Table 1. While the differences of coupling constant between cis- and trans-substituents on three-carbon bridge in this bicyclic system are small (ca. 0.2-0.3 Hz), the differences between corresponding geminal dimethyl groups are in the range of ca. 0.8-1.2 Hz. Thus, as in the case of olefins, all the coupling constants of trans-isomers are larger than that of the corresponding cis-isomers.

In conclusion, the small difference of one bond $^{13}$C-$^{13}$C coupling constant, which is large enough to be observed by the modern high field NMR, could be a useful alternative method for the stereochemical investigation when these derivatives could not be induced to use other NMR methods.

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<tr>
<th>Table 1. Observed hydrocarbons and their one-bond $^{13}$C coupling constants ($^{13}$C-13)</th>
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<tbody>
<tr>
<td>1. H$<em>{3}$C-CH$</em>{2}$-OH</td>
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<td>5. H$<em>{3}$C-CH$</em>{2}$-Cl</td>
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<tr>
<td>9. H$<em>{3}$C-CH$</em>{2}$-Cl</td>
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**References**