One-bond ^{13}C-^{13}C Coupling Constants for the Stereochemistry of Hydrocarbons

Chan-Jo Park, Gee-Chung Han, and Sueg-Geun Lee*

Chemical Analysis Lab., Korea Research Institute of Chemical Technology P.O. Box 107, Yusung, Taejeon 305-606, Korea

Received July 25, 2000

One-bond ^{13}C-^{13}C coupling constant has played a very important role in elucidation of the carbon skeleton of organic molecules.[1] 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.[2] 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.[3]

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.[4] 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.[5] Only a few stereospecifities of couplings are observed such as axial and equatorial bonds in ^{13}C-1-methyl-*cis*-1,4-dimethylcyclohexane and its *trans* isomer at about 180 K[6] and series of mono- and di-substituted cyclopropanes, where greater coupling constants have been found in *trans* substituted compounds.[7] 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,[3] 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 stereochemical 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, $90^\circ - \tau - 180^\circ - \tau - 90^\circ - \Delta - 90^\circ$, provided by Bruker, was used to measure ^{13}C-^{13}C cou-

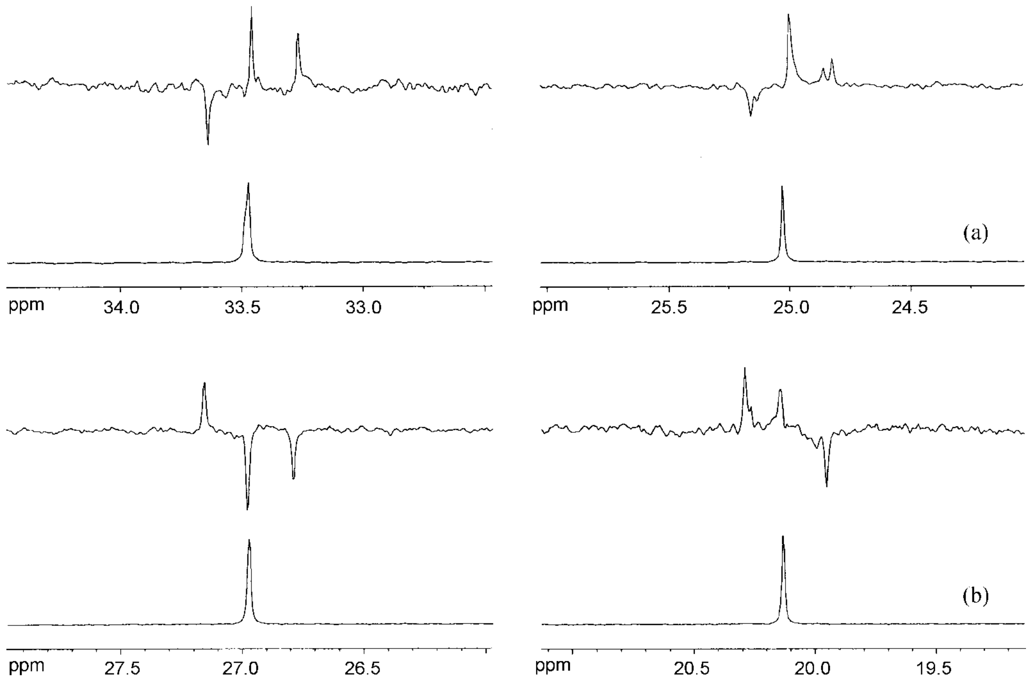


Figure 1. The expanded partial 1D-INADEQUATE spectrum of (a) *trans*- and (b) *cis*-1-bromo-2-pentene (**7**). Bruker AMX-500 spectrometer, 3 M in $CDCl_3$, relaxation delay 3 s, 10240 scans. The data were acquired with 64 K data points multiplied by exponential (LB=1.5).

pling constants.[8] The value of τ, which varied the amount of double quantum, was not optimized. Thus, the τ value used for all INADEQUATE experiments was 6.25 ms ($J = 40$ Hz). The 1D-INADEQUATE spectra were collected with 2-3 s relaxation delay and 64 K data point over *ca.* 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 polynominal 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.

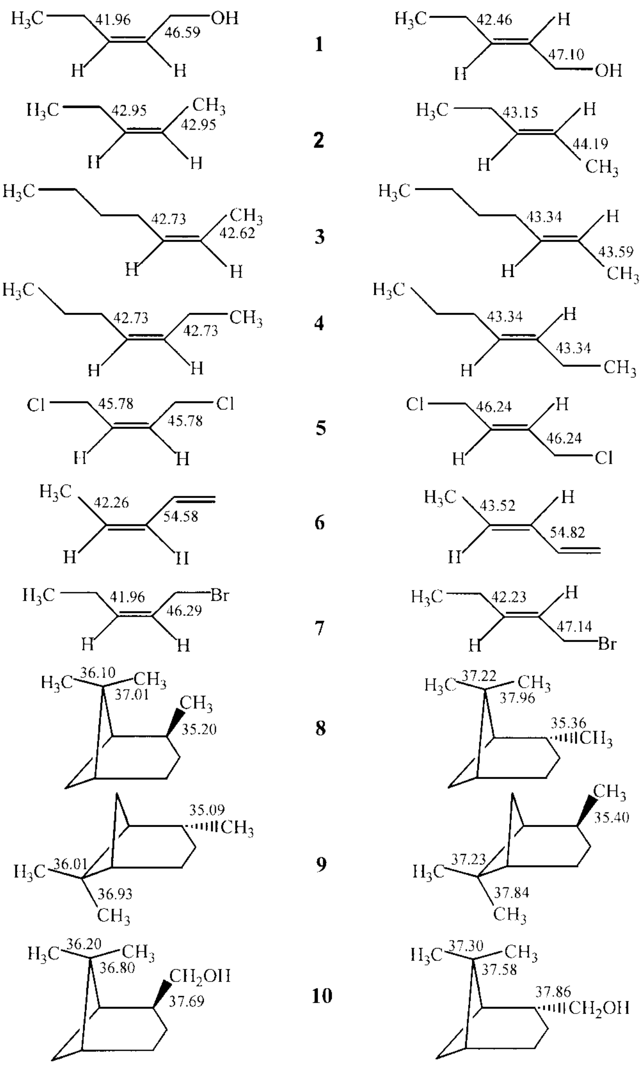
Results and Discussion

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 imines,[4,5] 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,[3] 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-dimethylcyclohexane, where the coupling constant of equatorial bond is *ca.* 0.8 Hz larger than that of axial bond.[6] As can be seen in the compounds **5** and **7**, the electronagativity 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,[9] 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.

Table 1. Observed hydrocarbons and their one-bond ^{13}C coupling constants ($^1J_{\text{C-C}}$)



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.

References

1. Kalinowski, H. O.; Berger, S.; Braun, S. *Carbon-13 NMR Spectroscopy*; John Wiley & Sons: New York, 1984; Chapter 4 and references cited therein.
2. (a) Lee, S.-G. *Bull. Korean Chem. Soc.* **1993**, *14*, 156. (b) Martin, G. E.; Zektzer, A. S. *Two-Dimensional NMR Methods for Establishing Molecular Connectivity*; VCH publisher: 1988; Chapter 5 and references cited therein.
3. Kamienska, T. K. In *Isotopes in the Physical and Biomedical Sciences*; Buncel, E., Jones, J. R., Eds.; Elsevier: New York, 1991; Vol. 2, Chapter 6.
4. Krivdin, L. B.; Kalabin, G. A.; Nesterenko, R. N.; Trofinmov, B. A. *Tetrahedron Lett.* **1984**, *25*, 4817.
5. Seo, E.-J.; Kim, K.-Y.; Lee, S.-G. *Bull. Korean Chem. Soc.* **1994**, *15*, 911.

6. Booth, H.; Everett, J. R. *Can. J. Chem*. **1980**, *58*, 2709.
7. Stocker, M.; Klessinger, M. *Liebigs. Ann. Chem*. **1979**, 1960.
8. Bax, A.; Freeman, R.; Frenkiel, T. A. *J. Am. Chem. Soc*. **1981**, *103*, 2102.
9. Kim, K.-Y.; Lee, S.-G. *Magn. Res. Chem*. **1997**, *35*, 451 and references cited therein.