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Directly Bonded Carbon-Hydrogen Coupling Constants of *n*-Pentane

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The values of the directly-bonded carbon-hydrogen coupling constants (J_{C-H}) of the methyl and methylene groups in *n*-pentane were calculated by using the CNDO/2 method, taking into account its rotational isomers, and it was found that the calculated values of J_{C-H} agree closely with the observed values.

The groundwork for the theoretical evaluation of spin-spin coupling constants was first laid by Ramsey *et al.*,[1,2] and since then several authors[3-7] have developed the valence-bond or molecular-orbital theory for the spin-spin coupling constants, using the average excitation energy (ΔE), based on Ramsey's theory. Then, on the basis of those theories, the correlation between the observed, directly-bonded carbon-hydrogen spin-spin coupling constant, J_{C-H}, and the degree of hybridization of the carbon atom in various compounds has been studied.[8-18] Recently Maciel *et al.*[19] have also interpreted the observed J_{C-H}'s of a number of compounds using finite pertubation techniques[20] which they have developed. However, in these studies there has been scarcely no study of the J_{C-H} values of molecules which have the various rotational isomers in liquids. In this paper, we will consider the relation between the experimental and the calculated carbon-hydrogen spin-spin coupling constants of the methyl and methylene groups of *n*-pentane, which can take various rotational isomers, and will also study their temperature dependences, using the CNDO/2 (Complete Neglect of Differential Overlap) method[21] as the molecular-orbital method.

Experimental

The carbon-13 NMR spectra of *n*-pentane were measured by means of a Japan Electron Optics Laboratory JEOL PS-100-type spectrometer at 25.15 MHz, at −60 and 22°C, using a 8 mm sample tube and the multiple-scan-average technique. Cyclohexane was used as the external referencee.

Calculation

From the molecular orbital theory[3-5] of nuclear spin-spin coupling constants, it can be shown that, if the Fermi contact term dominates the spin-spin coupling interaction, the magnitude of the coupling constant between directly-bonded nuclei should show a direct dependence on the amount of *s* character in the bond between them as follows:

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$$J_{\text{C-H}} = \left(\frac{4}{3}\right)^2 h\beta^2\gamma_{\text{C}}\gamma_{\text{H}}(\Delta E)^{-1}(1s_{\text{H}}|\delta|1s_{\text{H}})(2s_{\text{C}}|\delta|2s_{\text{C}})P^2_{\text{C-H}} \qquad (1)$$

where β is the Bohr magneton; γ_X, the nuclear magnetogyric ratio of the X atom; ΔE, the average excitation energy; $(1s_H|\delta|1s_H)$ and $(2s_C|\delta|2s_C)$, the one-electron integrals at the hydrogen and carbon nuclei respectively, and $P_{\text{C-H}}$, the carbon 2*s*-hydrogen 1*s* element of the bond-order matrix. Moreover, when 0.550 and 2.767 a.u.[22] are used as $(1s_H|\delta|1s_H)$ and $(2s_C|\delta|2s_C)$ respectively, Eq. (1) can be simply rewritten as follows:

$$J_{\text{C-H}} = 7885(\Delta E)^{-1}P^2_{\text{C-H}}\ (\text{Hz}) \qquad (2)$$

If the value of ΔE is a constant for each carbon of *n*-pentane, $J_{\text{C-H}}$ should be proportional to $P^2{}_{\text{C-H}}$. Here, the bond orders were calculated using the CNDO/2 method.

Among the nine rotational isomers, *n*-pentane can take seven preferred rotational isomers, the TT, TG, TG′, GT, G′T, GG, and G′G′ forms, but for the GG′ and G′G forms, which are at any rate, negligible because of their steric hindrances. The rotational isomeric states of *trans* (T) and *gauche* (G and G′) are defined as occurring at the rotational angles of 0, 120, and 240° respectively by means of the clockwise rotation around the C–C bond expressed in the Newman projection.

We numbered the carbon atoms in pentane as follows:

$$\text{CH}_3(1)\text{-CH}_2(2)\text{-CH}_2(3)\text{-CH}_2(2)\text{-CH}_3(1)$$

The C–C and C–H bond lengths are set as 1.54 Å and 1.10 Å respectively, and both the C–C–C and C–C–H bond angles are set at 109°28′.[23]

The numerical calculations were carried out by means of the HITAC-5020E of the Computer Center of the University of Tokyo.

Results and Discussion

The carbon-13 NMR spectrum of *n*-pentane observed at 22°C is shown in Fig. 1, where a quartet and two triplets are identified as $\text{CH}_3(1)$, $\text{CH}_2(2)$, and $\text{CH}_2(3)$ carbons respectively with a decrease in the field. Then, the directly-bonded carbon-hydrogen coupling constants ($J_{\text{C-H}}$) were obtained; they are shown in Table 1, including those values observed at −60°C. From these results, it was found that the $J_{\text{C-H}}$ value of the $\text{CH}_3(1)$ is larger than that of the $\text{CH}_2(2)$ or $\text{CH}_2(3)$, and that the $\text{CH}_2(2)$ is slightly larger than the $\text{CH}_2(3)$, but no value of $J_{\text{C-H}}$ depends upon the temperature.

Next, the calculated values of $P^2{}_{\text{C-H}}$ of seven rotational isomers in *n*-pentane are shown in Table 2, which also gives those values averaged by the populations of these rotational isomers using the following formula:

$$P^2_{\text{C-H}_{\text{AV}}} = \sum_{i=1}^{7} X_i P^2_{\text{C-H}_i} \qquad (3)$$

where;

$$X_i = e^{-\Delta E_i/RT} \Big/ \sum_{i=1}^{7} e^{-\Delta E_i/RT} \qquad (4)$$

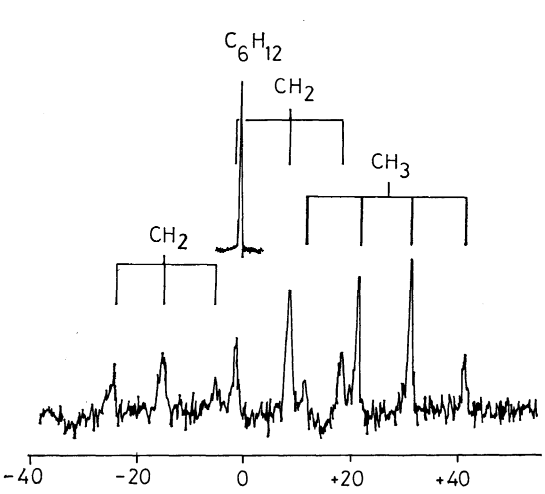

Fig. 1. The carbon-13 NMR spectrum of *n*-pentane in neat liquid at 22°C (128 scans). The reference is cyclohexane signal (proton spin-decoupled).

TABLE 1. THE OBSERVED AND CALCULATED VALUES OF $J_{\text{C-H}}$ IN *n*-PENTANE

Temperature	$J_{\text{C-H}}$ (Hz)		
	CH_3 (1)	CH_2 (2)	CH_2 (3)
Observed[a)]			
−60°C	127.6±0.5	124.6±0.5	122.9±0.5
22°C	127.8±0.5	124.8±0.5	122.6±0.5
Calculated[b)]			
ΔE= 10 eV			
−60°C	189.5	184.6	182.0
22°C	189.5	184.6	182.1
ΔE= 14.8 eV			
−60°C	127.8	124.7	122.9
22°C	127.8	124.7	123.1

a) Averaged using the four data.
b) Calculated using 570 cal/mol as ΔEg.

TABLE 2. THE CALCULATED VALUES OF $P^2_{\text{C-H}}$ IN THE PREFERRED ISOMERS AND THOSE AVERAGED OVER THE ISOMERS IN *n*- PENTANE

Conformations	$P^2_{\text{C-H}}$		
	$\text{CH}_3(1)$	$\text{CH}_2(2)$	$\text{CH}_2(3)$
TT	0.240	0.232	0.232
TG	0.240	0.231	0.230
TG′	0.240	0.231	0.230
GT	0.240	0.242	0.231
G′T	0.240	0.242	0.231
GG	0.240	0.229	0.228
G′G′	0.240	0.229	0.228
Averaged			
(a)	0.240	0.234_0	0.230_8
(b)	0.240	0.234_1	0.231_0

a) Averaged using 570 cal/mol as ΔE at −60°C.
b) Averaged using 570 cal/mol as ΔE at 22°C.

Here, $P^2{}_{\text{C-H}_i}$ is the square of the carbon 2*s*-hydrogen 1*S* element of the bond-order matrix, X_i, the fraction of the *i*-th isomer: ΔE_i, the energy difference between the TT and the *i*-th isomer; *R*, the gas constant, and

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T, the absolute temperature. Then, from Eqs. (2) and (3), the spin-spin coupling constant ($J_{C-H_{AV}}$) averaged by the populations of the rotational isomers is expressed as follows:

$$J_{C-H_{AV}} = \sum_{i=1}^{7} X_i J_{C-H_i}$$

$$= \frac{7885}{\Delta E}\sum X_i P^2_{C-H_i}$$

$$= \frac{7885}{\Delta E}\cdot P^2_{C-H_{AV}} \text{ (Hz)} \qquad (5)$$

where J_{C-H_i} is the spin-spin coupling constant of the i-th isomer. We have reported that the observed temperature dependence of the proton chemical shift of n-pentane can be better interpreted by 570 cal/mol as the energy difference (ΔEg) between the *trans* and *gauche* conformations.[24] Thus, 570 cal/mol was used as the ΔEg value of used in our calculations.[25]

The values of $J_{C-H_{AV}}$ calculated using 570 cal/mol as ΔEg are shown in Table 1. Since there is no definite value for the average excitation energy (ΔE) for n-pentane, we at first tried to use 10 eV for ΔE; this value was originally used by Pople[26] in the calculation of the C-13 chemical shift of ethane. The calculations were found to give much larger values than those observed. Then, as the observed values scarcely seem to depend upon the temperature, we determined ΔE using the method of least squares in such a way that the best agreement was between the calculated and observed values of J_{C-H} at −60 and 22°C; we found it to be 14.8±0.06 eV. By substituting this value into Eq. (5), $J_{C-H_{AV}}$ is expresses as:

$$J_{C-H_{AV}} = 533P^2_{C-H_{AV}} \qquad (6)$$

The plots of the observed J_{C-H} value against $P^2_{C-H_{AV}}$ are shown in Fig. 2. It was found that the J_{C-H} values of $CH_3(1)$, $CH_2(2)$, and $CH_2(3)$ are well proportional to those of P^2_{C-H}, calculated using 14.8 eV as ΔE. The solid line is the theoretical one obtained from Eq. (6). The scattering of the observed values from the theoretical line is found to be very small.

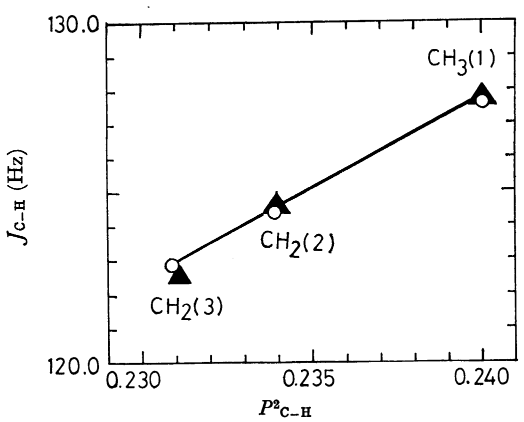

Fig. 2. The plots of the observed J_{C-H} against the P_{C-H}^2 in n-pentane. The solid line was calculated using Eq. (6). ○: observed at −60°C, ▲: observed at 22°C

As shown in Table 1, the temperature dependence of the values of J_{C-H} is not significant. Also, the calculated values of J_{C-H} depend scarcely at all upon the temperature, because the averaged values of P^2_{C-H} are not so sensitive to the temperature. However, this do not mean that it is not necessary to take the preferred conformations into account in the calculation of J_{C-H}. If the *trans* form is assumed to be the only conformation of n-pentane, the P^2_{C-H} values the $CH_2(2)$ and $CH_2(3)$ groups become equal to each other; therefore, the calculated and observed values of J_{C-H} do not agree with each other (the proportionality between J_{C-H} and P^2_{C-H} does not hold.). Thus, it is necessary to take the rotational isomers into account in order to obtain a better agreement with the observed and calculated results.

As has been described above, the same value, 14.8 eV, was used as ΔE for all the calculations of the J_{C-H} values of the methyl and methylene carbons in the preferred isomers; it was found to explain the experimental values reasonably well. However, there is a possibility that the ΔE values among the preferred isomer and among the carbons in a isomer differ from one another. Thus there remains some question about concluding 14.8 eV to be the ΔE of n-pentane. We will later treat with this problem in association with the carbon-13 chemical shifts of n-pentane.

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