BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 1040—1045 (1973)

The Proton Chemical Shift of *n*-Pentane

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(Received April 8, 1972)

The temperature dependence of the proton chemical shift of *n*-pentane was calculated by the CNDO/2 method, taking into account the possible preferred conformations and the contributions from the diamagnetic, paramagnetic, and bond anisotropy terms. It was found that the bond anisotropy term contributes predominantly, while the diamagnetic term is not negligible, and that the paramagnetic term is negligible in comparison with these terms. The observed temperature dependence of the chemical shift can be reasonably explained by calculations using 570 cal/mol as the energy difference between the *trans* and *gauche* conformations, and also using 9.1×10^{-30} cm^3 as the magnetic anisotropy of the C–C bond.

So far quantum-chemical calculations of the shielding constants in the chemical shifts of hydrocarbons have been done for some typical simple molecules, such as methane, acetylene, and ethylene,[1,2] by the LCAO MO method, but for more complex molecules which have some rotational isomers, *e. g.*, the *n*-pentane under consideration, these rigorous calculations becomes virtually impossible. Thus, for estimating the chemical shift of such molecules we must make some approximations by dividing the shielding constant into contributions from electrons localized on atoms and in the chemical bond.

According to Pople,[3] the shielding constant, σ_A, of a nucleus A is written as:

$$\sigma_A = \sigma_A^{\mathrm{dia}} + \sigma_A^{\mathrm{para}} + \sum_{B(\neq A)} \sigma_{AB} \qquad (1)$$

where the σ_A^{dia} term arises from induced diamagnetic currents on the A atom, depending upon the electron density around the nucleus, A; where σ_A^{para} is the contribution of induced paramagnetic currents on A, and where σ_{AB} is the contribution arising from locally-induced currents on the atoms, B's, other than A in the molecule, referred to as the neighbour anisotropy effect. In estimating these terms, we will use the electron density calculated by the CNDO/2 (Complete Neglect of Differential Overlap) method[4] for σ_A^{dia}, and will apply Marshall and Pople's theory[5] to the evaluation of σ_A^{para}, which is here assumed to be contributed by the excess or deficient charges on the carbon atom bonded to the specified proton; we will also calculate the bond anisotropy term[6] for σ_{AB}, because it is difficult to obtain exactly information about the excitation energy which is used in the point dipole equation.[3]

Many attempts using the LCAO MO method have been made to estimate the proton and the ^{13}C chemical shift of hydrocarbon molecules by calculating the electron density. Yonezawa *et al.*[7] calculated the electron densities on hydrogen atoms of hydrocarbons by the simple LACO MO method for the σ electron system, and estimated the chemical shifts. The calculated results are consistent with the observed ones, but the simple LCAO MO method is too simple for a discussion of the proton chemical shift of *n*-pentane, which can take various conformations. Sichel and Whitehead[8] calculated the electron density on atoms of hydrocarbons using the extended Hückel theory, which can take into account the molecular conformations; they found that the calculated electron densities on the carbon atoms correspond well to the observed ^{13}C chemical shifts, but that those on the hydrogen atom do not correspond to the proton chemical shift. Baird and Whitehead[9] discussed the correlation between the proton chemical shift of hydrocarbons and the electron density calculated by the electronegativity equation method, and found that the ^{13}C chemical shift reasonably corresponds to the charge on the carbon atom, while the proton chemical shift does not correspond to that on the hydrogen atom.

As has been described above, a good correlation between the calculated electron densities on the hy-

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drogen atoms and the chemical shifts of proton in hydrocarbons has not been obtained. One cause may be the neglect of the second and third terms in Eq. (1). In the proton chemical shift of nonpolar hydrocarbon molecules, it is usually conjectured that the contribution of the second term to the chemical shift is negligible in comparison with those of the other terms. Generally discussing the chemical shift of such molecules, we will report that the third term is important.

It is the purpose of this paper to calculate the proton chemical shift of *n*-pentane, considering the various conformations, and to estimate plausible values of the *trans-gauche* potential barrier and the magnetic bond anistropy of the C–C bond, $\Delta\chi_{C-C}$, by comparing the observed temperature dependences of the proton chemical shifts with the calculated ones.

Experimental

The NMR spectra of *n*-pentane (99.9%) were measured in neat liquid at temperatures from −70 °C to +60 °C, using a JEOL 4H-100 type spectrometer (100 MHz). Tetramethylsilane (TMS) was used as the internal standard. The chemical shift is expressed in ppm downfield.

Calculation

In estimating the chemical shift of *n*-pentane, we calculate separately the first, second, and third terms in Eq. (1).

The first term[10] is expressed as;

$$\sigma_A^{\rm dia} = \frac{e^2}{3mc^2} = \left<0\left|\sum_k \frac{1}{r_k}\right|0\right> \tag{2}$$

where e is the electron charge; *m*, the mass of the electron; *c*, the velocity of light, and r_k the distance of the *k*-th electron from the nucleus, and where $|0>$ refers to the electronic ground state of the molecule. $\sigma_A^{\rm dia}$ is fairly easy to calculate, since it depends only on the electron distribution in the electronic ground state. Thus, in practice, we used the following equation[3] to estimate the proton chemical shift;

$$\sigma_A^{\rm dia} = k \cdot \rho \tag{3}$$

where we used 17.8 ppm[3] as k and where ρ is the electron density of the atom under consideration, being calculated by the CNDO/2 method.

The second term, the paramagnetic one, which represents the effect of the mixing of the ground and excited states by the magnetic field, is usually more difficult to evaluate. Thus, we will evalute this term by the following expression, proposed by Marshall and Pople,[5] which was obtained from a calculation of the nuclear magnetic shielding in a hydrogen nucleus placed in an electric field, due to the excess or deficient charge on the carbon atom bonded to the hydrogen atom, neglecting any effect of the spin of the electron:

$$\sigma_A^{\rm para} = k \cdot \sigma_\perp^{\rm para} \sin^2\theta \tag{4a}$$

$$\sigma_\perp^{\rm para} = -\frac{233}{144}\frac{a^3E^2}{mc^2} \tag{4b}$$

where $\sigma_\perp^{\rm para}$ is the paramagnetic shielding constant in the case of H (magnetic field) perpendicular to E (electric field); $\sigma_A^{\rm para}$, the value of σ for an intermediate direction making an angle of θ with E, and a, the Bohr radius. Therefore, when we evaluate $\sigma_A^{\rm para}$, one must average all the θ angles. Thus, $\sigma_A^{\rm para}$ becomes:

$$\sigma_A^{\rm para} = \frac{1}{2}\sigma_\perp^{\rm para}$$

$$= -\frac{1}{2}\cdot\frac{233}{144}\frac{a^3E^2}{mc^2} \tag{5}$$

When we estimate E in any specified hydrogen nucleus, we assume that the hydrogen nucleus experiences the electric field of the carbon atom bonded to it, which arises from its excess electron charge.

As to the third term, although the point dipole equation proposed by Pople[3] should be used, it is difficult to estimate the equation because the excited states are not known. Thus, we used approximately the McConnell equation[6], neglecting only the small contribution from the C–H bond.

$$\sigma_{AB} = \frac{\Delta\chi_{C-C}}{3r^3}(1-3\cos^2\theta_M) \tag{6}$$

in which $\Delta\chi_{C-C}(=\chi_\parallel - \chi_\perp)$ is the magnetic anisotropy of the C–C bond, where r is the distance between any specified proton and the midpoint of the C–C bond, and where θ_M is the angle between the directions of r and the C–C bond. So far, although various values for the magnetic anisotropy of the C–C bond have been reported,[11] the most reliable value is not known at present. However, to promote the discussion, we adopted tentatively the value of 5.5×10^{-30}cm^3 reported by Bothner-By and Narr-Colin.[11] We will discuss the value of $\Delta\chi_{C-C}$ in a later chapter.

Here, the rotational isomeric states of *trans*(T) and *gauche* (G and G′) are defined to occur at the rotational angles about 0°, 120°, and 240° respectively by the clockwise rotation around the C–C bond as expressed in the Newman projection.

We numbered the carbon atoms in pentane as follows:

$$CH_3(1)\text{-}CH_2(2)\text{-}CH_2(3)\text{-}CH_2(4)\text{-}CH_3(5)$$

The C–C and C–H bond lengths are set as 1.54 Å and 1.10 Å respectively, and both of the C–C–C and C–C–H bond angles are set at 109°28′.[12]

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

Results and Discussion

n-Pentane can take seven isomeric states (TT, TG, TG′, GT, G′T, GG and G′G′), where GG′ and G′G were ignored due to the large steric hindrance. Because the observed chemical shift is usually considered to be the average of the chemical shifts of rapidly interconverting rotamers, the chemical shift, $\sigma(j)$, of the *j*-th proton in *n*-pentane should be expressed as follows:

$$\sigma(j) = \sum_{i=1}^{7} X_i \sigma_i(j) \tag{7}$$

where X_i and σ_i are the fraction and the chemical shift of the *i*-th isomer respectively. X_i is expressed as:

$$X_i = e^{-\Delta E_i/RT} / \left(\sum_{i=1}^{7} e^{-\Delta E_i/RT} \right) \tag{8}$$

where *R* is the gas constant; *T*, the absolute temperature, and ΔE_i the energy difference between TT and the *i*-th conformation.

Now, let us discuss the electron-density distributions of *n*-pentane in Fig. 1, we show the electron densities of the protons in the TT, TG and GG conformations as obtained by the CNDO/2 method; one of the three protons of the methyl group is assumed to take the *trans* position in relation to the central carbon atom. The electron density of the methyl protons is averaged by the three protons in the methyl group, since it may be considered that the methyl group rotates freely, and the parameters used in the CNDO/2 calculation are the same as those proposed by Pople.[4] The electron densities of the protons in the other conformations can be at once obtained from those of the TT, TG and GG conformations. The calculated total energies of these conformations were −1221.4326, −1221.4136, and −1221.3698 eV respectively. Thus, the energy difference between the *trans* and *gauche* conformations, ΔE_g, is *ca.* 440 cal/mol in an isolated pentane. This agrees fairly well with the value (450±60 cal/mol) obtained by the spectroscopic method,[13] the value (*ca.* 500 cal/mol) obtained by an inherent bond potential, and the energy of interaction between nonbonded substituents.[14] This is one of several successful cases[15] of the application of the CNDO/2 method to problem of the energy difference between the rotational isomers. Recently Fujiyama *et al.*[16] reported obtaining a value of 600 cal/mol by laser-Raman spectroscopy, and Ishikawa and Nagai.[17] obtained *ca.* 800 cal/mol by means of the electro-optical effect. Our value is more or less lower than the experimental ones shown above. We will discuss this point below.

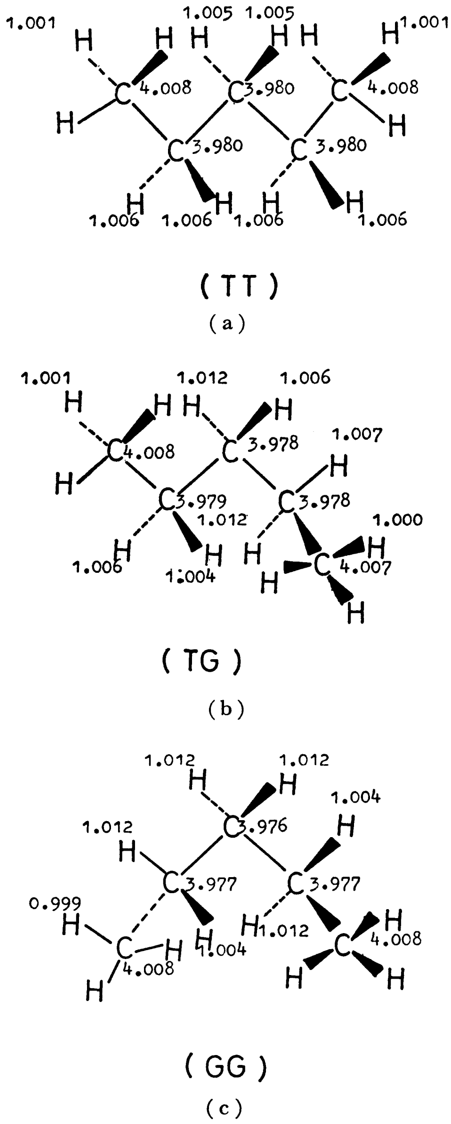

Fig. 1. The electron densities on the atoms of *n*-pentane in (a) TT, (b) TG, (c) GG conformations.

The temperature dependences of the proton diamagnetic shielding constants calculated by using Eqs. (3), (7), and (8) are shown in Fig. 2, in which the 440 and 600 cal/mol obtained by the CNDO/2 method and the laser-Raman spectroscopy respectively as described above are used as ΔE_g, and in which the $CH_2(2)$ and the $CH_2(4)$ are equivalent to each other. For reference, the values at 22°C are listed in Table 1. The temperature dependences of the chemical shifts calculated with 440 and 600 cal/mol as ΔE_g differ considerably from each other; the finding that the methyl protons are less shielded than the methylene groups is opposite to the observed one, as is shown in Fig. 3. This is true over a wide temperature range, as is shown in Fig. 4. Thus, the proton chemical shift of *n*-pentane cannot be explained by the first term only, but it is noticeable that there is a small and detectable chemical shift between the $CH_2(2)$

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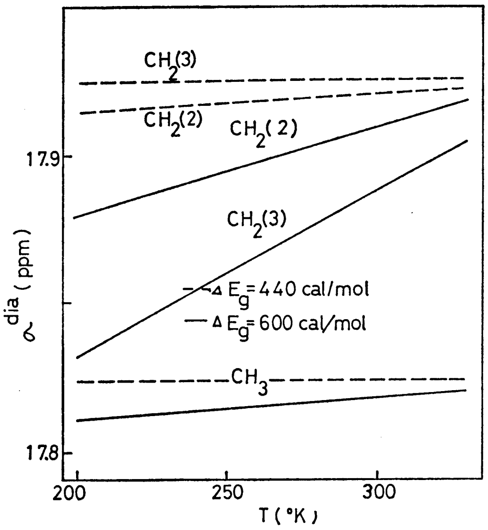


Fig. 2. The temperature dependences of the diamagnetic shielding term of *n*-pentane used 440 cal/mol and 600 cal/mol as ΔE_g.

Table 1. The diamagnetic shielding term σ^{dia} magnetic anisotropy effect term $\sigma_{\mathrm{C-C}}$ and their sum σ of *n*-pentane at 22 °C

	σ^{dia} (ppm)	$\sigma_{\mathrm{C-C}}$ (ppm)	σ (ppm)
ΔE_g=440 cal/mol			
$CH_3(1)$	17.825	−0.308	17.517
$CH_2(2)$	17.925	−0.588	17.337
$CH_2(3)$	17.926	−0.549	17.377
ΔE_g=600 cal/mol			
$CH_3(1)$	17.818	−0.306	17.512
$CH_2(2)$	17.910	−0.601	17.309
$CH_2(3)$	17.880	−0.538	17.342

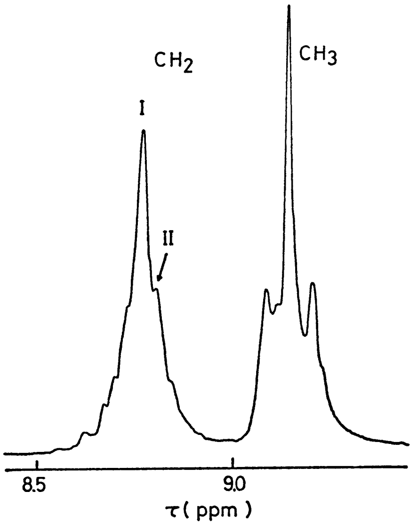
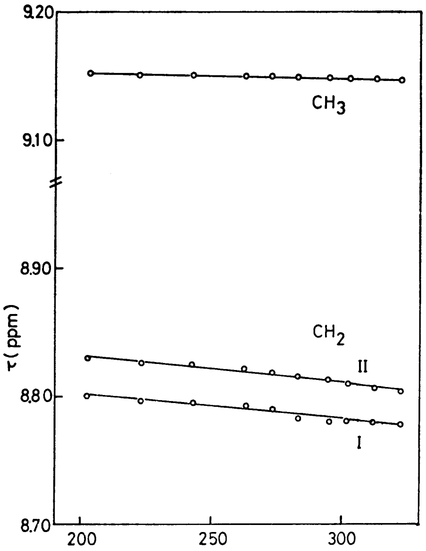


Fig. 3. The NMR spectrum of *n*-pentane. (at 22 °C and 60 MHz).

and $CH_2(3)$ protons in this calculation.

The second term, the paramagnetic contribution, was calculated according to Eq. (4), estimating *E* at any specified proton by the excess or deficient charge from the neutral one at the carbon atom bonded to the proton; the results are shown in Table 2. As expected, the contribution of the paramagnetic term to the proton chemical shift of *n*-pentane is almost negligible in comparison with the diamagnetic one shown in Table 1. It may be considered that the formation of the *S*-state electron localized around the hydrogen nucleus resulting from the adjacent carbon atom, is very small in *n*-pentane. Thus, we may neglect this term.



T (K)

Fig. 4. The temperature dependence of the observed chemical shift of *n*-pentane.

Table 2. The paramagnetic term σ^{para} of the TT, TG and GG conformations of *n*-pentane.

Preferred conformation	TT (ppm)	TG (ppm)	GG (ppm)
$CH_3(1)$	−0.00029	−0.00029	−0.00029
$CH_2(2)$	−0.00180	−0.00179	−0.00243
$CH_2(3)$	−0.00180	−0.00226	−0.00265
$CH_2(4)$	−0.00180	−0.00220	−0.00243
$CH_3(5)$	−0.00029	−0.00023	−0.00029

Next, we shall discuss the third term, which was calculated by assuming the C–C bond anisotropy effect. The results obtained are shown in Fig. 5, in which 440 and 600 cal/mol are used as ΔE_g. It has been found that the order of the arrangement of the calculated chemical shifts of each proton agrees fairly well with those observed over a wide temperature range, the temperature dependences of the chemical shifts of the CH_3 and $CH_2(2)$ groups differing from each other, and the contribution of this term to the chemical shift of *n*-pentane is larger than that of the diamagnetic term. Then, summing up σ^{dia} and $\Delta\chi_{\mathrm{C-C}}$ contributions, we obtained the results shown in Figure 6. For reference, the sum of both contributions at 22 °C is listed in Table 1, which reveals that the chemical shifts of the $CH_2(2)$ and $CH_2(3)$

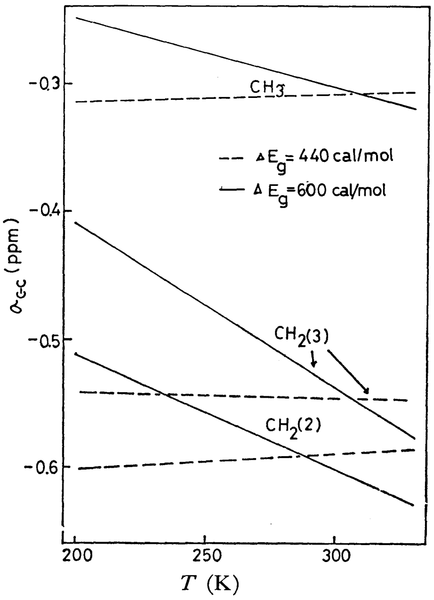


Fig. 5. The temperature dependence of the bond anisotropy term used 440 and 600 cal/mol as ΔE_g.

differ from each other slightly. The spectrum shown in Figure 3 suggests that the signal of the CH_2 group shows a weak shoulder, II,[18] on the higher-field side of the main peak, I, with a chemical-shift difference of 0.058 ppm, and that the ratio of the intensities of the peaks, I to II, is about 2 : 1. Moreover, it is found that the calculated temperature dependences of the chemical shifts for CH_3, $CH_2(2)$, and $CH_2(3)$, shown in Fig. 6, correspond qualitatively to those of these peaks, I and II, which shift to a lower field with an increase in the temperature. Comparing these observed and calculated results, it may tentatively be assumed that the peaks, I and II, are assignable to the $CH_2(2)$ and $CH_2(3)$ groups respectively. However, taking into account the effect of the spin-spin coupling, this assignment is more or less tentative; a detailed and more reliable assignment of these protons could be obtained by using some deuterated compounds and spectrum simulation.

As may be seen from Table 1, the chemical shifts between the CH_3 and $CH_2(2)$ groups in the cases of ΔE_g=440 cal/mol and 600 cal/mol are 0.180 and 0.210 ppm respectively, and those between the CH_3 and $CH_2(3)$ groups in the cases of ΔE_g=440 and 600 cal/mol are 0.140 and 0.170 ppm respectively. The quantitative agreement between the observed and the calculated values is not good. As to the temperature dependence of the chemical shift, it is found that the sign of the slope of the chemical shift of the $CH_2(3)$ group calculated using 440 cal/mol as ΔE_g coincides with that observed, while those of the CH_3 and $CH_2(2)$ groups do not, and that those of the CH_3, $CH_2(2)$ and $CH_2(3)$ groups derived by taking 600 cal/mol as ΔE_g coincide with those observed. Thus, the results calculated for 600 cal/mol agree with the observed values better than those calculated for 440 cal/mol in neat liquid. This is natural because 440 cal/mol for ΔE_g is the value calculated in an isolated *n*-pentane molecule. From these calculations, it may be seen that the slopes of the chemical shifts against the temperature depend on the magnitude of ΔE_g. For discussing the slope and ΔE_g, we plotted the observed and calculated chemical-shift differences between the CH_3 and $CH_2(2)$ groups ($\Delta\sigma_{CH_3-CH_2(2)}$) and the CH_3 and $CH_2(3)$ ($\Delta\sigma_{CH_3-CH_2(3)}$) against the temperature in Fig. 7. This figure also shows that 600 cal/mol is better than 440 cal/mol for ΔE_g. The

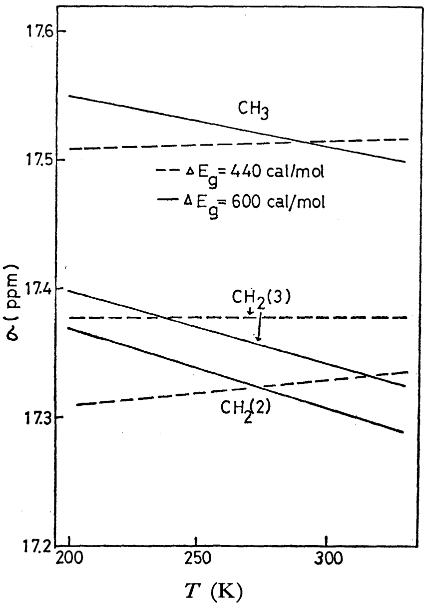


Fig. 6. The temperature dependence of the sum of the diamagnetic and the bond anisotropy terms used 440 and 600 cal/mol as ΔE_g.

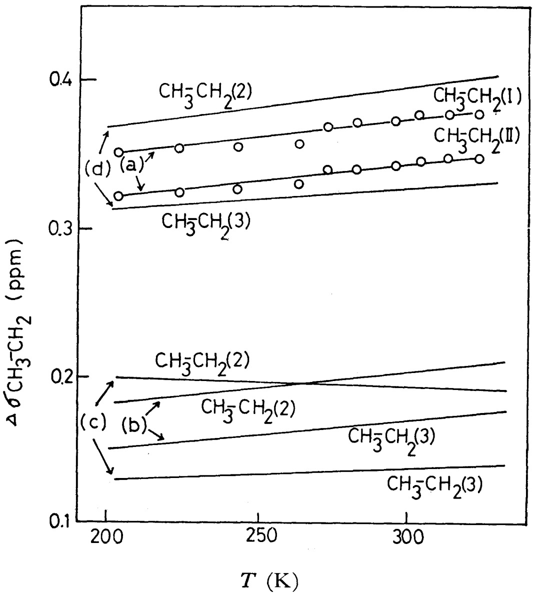


Fig. 7. The temperature dependence of the chemical shift difference between the CH_3 and CH_2 (2) groups.
(a) observed. (b) calculated with 440 cal/mol and (c) 600 cal/mol for ΔE_g, and 5.5×10^{-30} cm³ for $\Delta\chi_{C-C}$. (d) calaclated with 570 cal/mol for ΔE_g and 9.1×10^{-30} cm³ for $\Delta\chi_{C-C}$.

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[18] This peak splits more clearly in benzene, pyridine and α-chloronaphthalene than in this case (neat liquid).

best-fitting calculated slope to the observed one can be obtained by taking 570 cal/mol for ΔE_g, as is shown in Fig. 7(c), but the quantitative agreement between the chemical shifts observed and calculated is not satisfactory. The discrepancy may be caused by our choice of the value of $\Delta\chi_{C-C}$. As may be seen from Figure 8, the observed chemical shift differences $\Delta\sigma_{CH_3-CH_2}$ $(=\sigma_{CH_3}-\sigma_{CH_2})$ can be fitted by choosing 8.5—9.7$\times 10^{-30}$ cm^3 as $\Delta\chi_{C-C}$. Thus, using 9.1$\times 10^{-30}$ cm^3 at its averaged value of $\Delta\chi_{C-C}$ and 570 cal/mol as ΔE_g, the calculated temperature dependence of the chemical shift difference, $\Delta\sigma_{CH_3-CH_2}$, is shown in Fig. 7(d). It is found that the calculated results agree fairly well with the observed ones. However, the chemical-shift difference between the CH_2(2) and CH_2(3) groups disagrees slightly. We consider that this is partly due to the ambiguity of the assignment of the CH_2 (II) group. It is necessary to use some deuterated compounds and to simulate the NMR spectrum, taking the spin-spin coupling into account, in order to obtain a more reliable assignment. The above value of $\Delta\chi_{C-C}$, 9.1$\times 10^{-30}$ cm^3, is near to the value, 10.0$\times 10^{-30}$ cm^3, proposed by Moritz and Shappard.[11f] However, Homer and Callaghan[11] reported 7.26$\times 10^{-30}$ cm^3 as the $\Delta\chi_{C-C}$ value of the magnetic anisotropy, but neglected the effect of electron density. If we neglect the contribution of the diamagnetic effect in order to fit the observed results with the calculated ones, we obtain 7.0$\times 10^{-30}$ cm^3 as $\Delta\chi_{C-C}$. This value is nearly equal to that proposed by Homer and Callaghan. However, we consider that it is better to adopt 9.1$\times 10^{-30}$ cm^3 as $\Delta\chi_{C-C}$ in *n*-pentane because the diamagnetic contribution to the chemical shift depends upon the conformation.

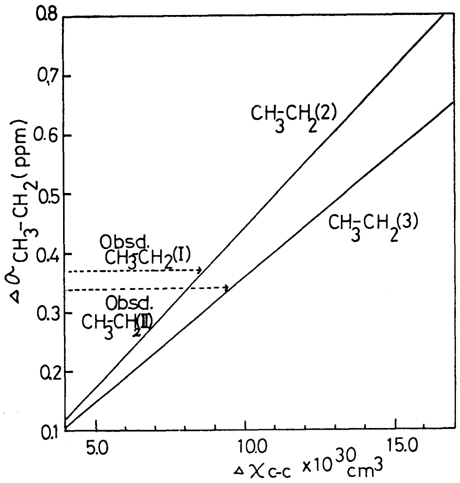

Fig. 8. The chemical shift dependences (CH_3–CH_2 (2) and CH_3–CH_2 (3)) on $\Delta\chi_{C-C}$. ---→: observed results.

The authors gratefully acknowledge the helpful comments made by Dr. N. Nakagawa of the University of Electro-Communication and by Dr. T. Yonemoto of the Electrotechnical Laboratory, and the use of the program of the CNDO/2 method made by Dr. T. Hirano of the University of Tokyo.