Proton Nuclear Magnetic Resonance Spectroscopy of Partially-deuterated *n*-Pentanes

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The proton NMR spectra of some partially deuterated *n*-pentanes were observed under both proton-deuteron (H–D) spin-coupled and -decoupled conditions. With using the spectrum-simulation method, it was confirmed experimentally that the chemical shift of the $CH_2(3)$ protons appears at a higher field than that of the $CH_2(2)$ protons.

It is well known[1] that, in the case of molecules with rotational isomers, in which rotation about the C–C bond is very quick, the observed NMR chemical shift is averaged with the statistical weight for each isomer. *n*-Pentane can take seven preferred isomeric forms[2] (TT, TG, GT, TG′, G′T, GG, G′G′), while GG′ and G′G conformations are ignored because of the steric hindrance or the so-called "pentane effect." In a previous paper,[3] the proton NMR chemical shift of *n*-pentane has been calculated theoretically, taking into account the above conformations, and then the energy difference between *trans* and *gauche* conformations and the magnetic anisotropy of the C–C bond was estimated. According to the results obtained there, the $CH_2(3)$ proton peak would appear at a field higher than that of the $CH_2(2)$ proton by 0.03—0.04 ppm.

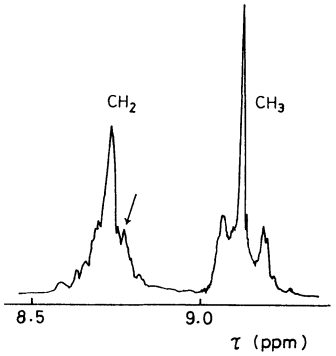

Fig. 1. The proton NMR spectrum of non-deuterated *n*-pentane in CCl_4 solution at 22.5 °C. The chemical shift of methyl protons appears at 9.125τ. The shoulder of the $CH_2(3)$ proton is indicated by an arrow.

As is shown in Fig. 1, the observed spectrum of the methylene groups in *n*-pentane has a weak shoulder at a higher field in the main peak. This shoulder was previously tentatively assigned to the $CH_2(3)$ protons, and the main peak, to the $CH_2(2)$ protons.[3] Such an assignment, however, was made without taking into account the effect of the nuclear spin-spin coupling. Since the difference in the chemical shift between the $CH_2(2)$ and $CH_2(3)$ protons is very small, it may be considered that the spin-spin coupling plays an important role in determining the pattern of the spectrum. Hence, we attempted to confirm whether the previous assignment is true or not. In doing this, we may encounter inconvenience due to the large number of protons. Therefore, we prepared some partially-deuterated *n*-pentanes and made spectrum-simulation in order to determine whether or not the chemical shift of the $CH_2(3)$ protons appears at a field higher than that of the $CH_2(2)$ protons.

Experimental

Materials. The partially-deuterated *n*-pentanes, (II)—(V), used here are as follows:

$CH_3CH_2CH_2CH_2CH_3$ (I)

$CH_2DCH_2CH_2CH_2CH_2D$ (II)

$CHD_2CH_2CH_2CH_2CHD_2$ (III)

$CD_3CH_2CH_2CH_2CD_3$ (IV)

$CH_3CH_2CD_2CH_2CH_3$ (V)

They were prepared by the method to be described below.

Preparation. $CD_3CH_2CH_2CH_2CD_3$: Dimethyl glutarate (25 g) was added, drop by drop, to a well-stirred solution of lithium aluminum deuteride (7 g) in dry ether (150 ml). After this addition and stirring for 2 hr, the excess lithium aluminum deuteride was carefully decomposed with water to give a product like white clay. 1,5-Pentanediol-1,1,5,5-d_4 (12 g) was extracted from the product with ether by using a Soxhlet extractor for 2 days. The ether was then evaporated, and the resulting alcohol was treated with potassium iodide (50 g) in a mixture of phosphoric anhydride (12 g) and 85% phosphoric acid (40 ml) to give 1,5-diiodopentane-1,1,5,5-d_4. After drying, it was converted to *n*-pentane-1,1,1,5,5,5-d_6 with heavy water by the usual Grignard reaction. This product (*ca.* 1 ml) was separated from ether by washing with cold, concentrated sulfuric acid, and then distilled. The NMR spectrum of the deuterated *n*-pentane showed the absence of methyl protons.

$CH_3CH_2CD_2CH_2CH_3$: Diethyl ketone (25 g) was reduced with lithium aluminum deuteride (3 g) in dry ether (100 ml) in the usual way to give 3-pentanol-3-d_1 (14 ml). A mixture of this alcohol and freshly-distilled methanesulfonyl chloride in methylene chloride (70 ml) was treated with pyridine (15 ml) below −5 °C. After having been stirred for 1 hr in an ice-salt bath, the mixture was stored in a refrigerator for 24 hr and then poured into dilute sulfuric acid. The washed and dried organic layer was evaporated at room temperature, and the residue was pumped for several hours to yield 3-penthyl-3-*d* methanesulfonate (13 ml). This product was added, drop by drop, to a solution of lithium aluminum deuteride (4 g) in dry ether (100 ml). A mixture of *n*-pentane-3,3-d_2 and ether was distilled, and the deuterated *n*-pentane (2 ml) was separated from ether by washing with cold concentrated sulfuric acid. According to the NMR spectrum of this product, the deuterium content was more than 95%.

Method: The proton NMR spectra of partially-

deuturated *n*-pentanes were measured by means of a JEOL PS-100-type spectrometer at 100 MHz, in a solution of carbon tetrachloride at room temperature. Tetramethylsilane (TMS) was used as the internal standard. The deuteron spin decoupling (D-decoupling) was done using JNM SD-HC (hetero spin decoupler) equipment.

Calculations of the NMR spectra were carried out by means of the HITAC 5020E of the Computer Centre of the University of Tokyo, using a LAOCOON III program.

Results and Discussion

The observed spectra of some deuterated *n*-pentanes are shown in Figs. 2, 3, 4, and 5, where (a) and (b) were obtained under proton-deuteron (H–D) spin-coupled and -decoupled conditions respectively. The following features may be noted: In *n*-pentane-1,5-d_2, $CH_2DCH_2CH_2CH_2CH_2D$ (II), each line of the methyl proton triplet, moreover, splits into a triplet (Fig. 2(a)) as a result of the geminal H–D spin-spin coupling, the constant of which is $J_{H\text{-}D}^{gem}=1.9$ Hz. In *n*-pentane-1,1,5,5-d_4, $CHD_2CH_2CH_2CH_2CHD_2$ (III), it splits into a quintet (Fig. 3(a)). While Fig. 4(a) shows only a single methylene proton peak, which is somewhat broad because of the vicinal H–D spin-spin coupling,

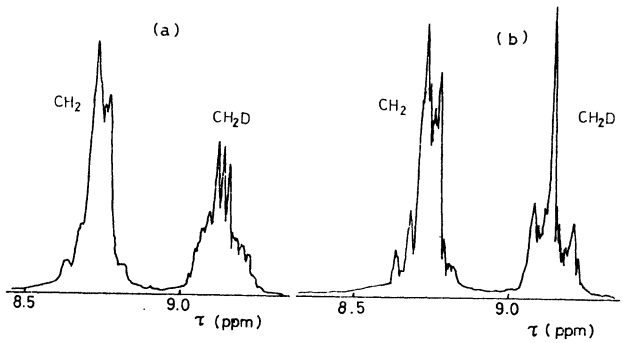

Fig. 2. The proton NMR spectrum of *n*-pentane-1,5-d_2 in CCl_4 solution at 22.5 °C. The chemical shift of methyl protons appears at 9.141τ.
(a) Taken under H–D spin-undecoupled condition.
(b) Taken under H–D spin-decoupled condition.

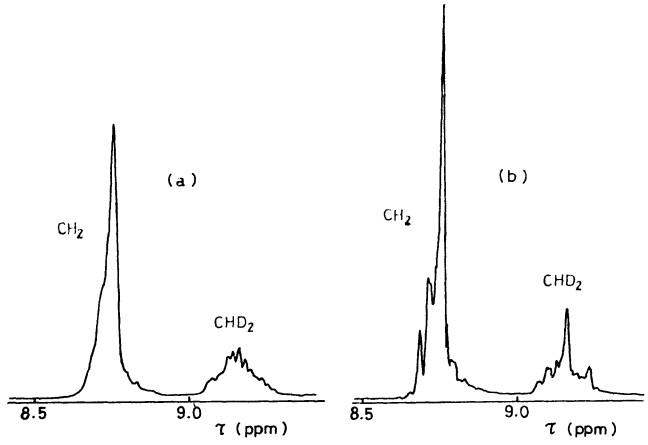

Fig. 3. The proton NMR spectrum of *n*-pentane-1,1,5,5-d_4 in CCl_4 solution at 22.5 °C. The chemical shift of methyl protons appears at 9.158τ.
(a) Taken under H–D spin-undecoupled condition.
(b) Taken under H–D spin-decoupled condition.

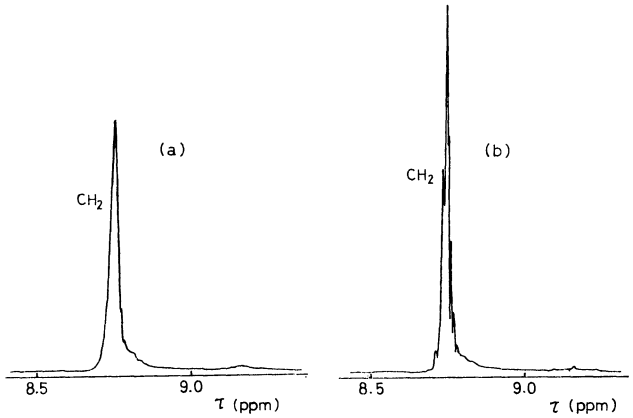

Fig. 4. The proton NMR spectrum of *n*-pentane-1,1,1,5,5,-5-d_6 in CCl_4 solution at 22.5 °C.
(a) Taken under H–D spin-undecoupled condition.
(b) Taken under H–D spin-decoupled condition.

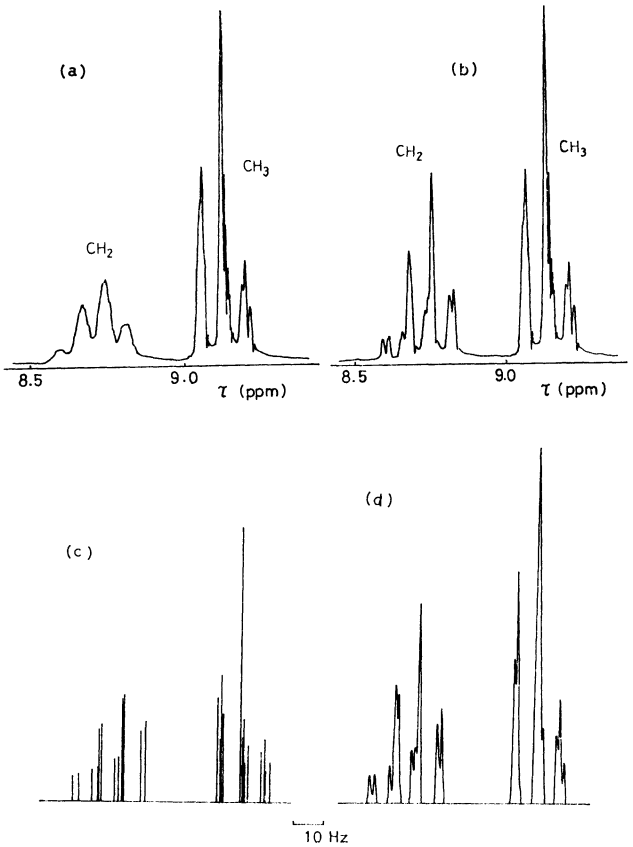

Fig. 5. The proton NMR spectrum of *n*-pentane-3,3-d_2 in CCl_4 solution at 22.5 °C. The chemical shift of methyl protons appears at 9.127τ.
(a) Taken under H–D spin-undecoupled condition.
(b) Taken under H–D spin-decoupled condition.
(c) Calculated "Stick" spectrum.
(d) Calculated spectrum in Lorentzian line shapes. with half-height-width of 0.4 Hz.

the D-decoupled spectrum (Fig. 4(b)) shows a fine structure, which may be expected to come from the chemical-shift difference between the methylene protons in *n*-pentane-1,1,1,5,5,5-d_6, $CD_3CH_2CH_2CH_2CD_3$ (IV). *n*-Pentane-3,3-d_2, $CH_3CH_2CD_2CH_2CH_3$ (V), gives a A_3B_2-type spectrum of the five-spin system (Fig. 5(b))

if the deuteron is irradiated. As is shown in Fig. 5(a), line broadening occurs in the methylene proton quartet because of the vicinal H–D spin-spin coupling, the constant of which is probably about 1 Hz, but the methyl proton triplet remains sharp. This means that the long-range H–D spin-spin coupling separated by more than four bonds is negligibly small.

As we have stated above, we are mainly concerned with the problem of the chemical-shift difference between the $CH_2(2)$ and $CH_2(3)$ protons, which was previously predicted by means of theoretical calculations.[3] Thus, let us first compare the spectra of the partially-deuterated *n*-pentane measured under two different conditions, in which one was under undecoupled conditions and the other, under D-decoupled conditions. As for Sample (II), a comparison between Figs. 2(a) and 2(b) shows the following features: the shoulders which appear on the down-field side of the methylene peak in Fig. 2(a), which may be expected to come from the line broadening due to the vicinal H–D spin-spin coupling, change into rather sharp peaks upon D-decoupling, as is shown in Fig. 2(b) but there is almost no significant difference on the up-field side. Also, in the case of Sample (III), similar features are noted in comparing the spectra shown in Figs. 3(a) and 3(b). The $CH_2(2)$ protons are placed on the vicinal position against the deuterium atom in the methyl group, while the $CH_2(3)$ protons are on the position of four-bond separation from the deuterium atom. We may, therefore, conclude qualitatively that the chemical shift of the $CH_2(2)$ protons should appear at a lower field than that of the $CH_2(3)$ protons: this is in agreement with the previous results.

TABLE 1. THE PARAMETERS USED IN DOING THE SPECTRUM SIMULATION OF DEUTERATED *n*-PENTANES

$CH_3CH_2CD_2CH_2CH_3$	
	$\delta_{CH_3(1)\text{-}CH_2(2)}=0.415$ ppm
	$J^{gem}_{CH_3(1)\text{-}CH_2(1)}=J^{gem}_{CH_3(2)\text{-}CH_2(2)}=12.4$ Hz
	$J^{vic}_{CH_3(1)\text{-}CH_2(2)}=7.4$ Hz
$CD_3CH_2CH_2CH_2CD_3$	
	$\delta_{CH_3(3)\text{-}CH_2(2)}=0.05$, 0.03, and -0.03 ppm
	$J^{gem}_{CH_3(2)\text{-}CH_2(2)}=J^{gem}_{CH_3(3)\text{-}CH_2(3)}=12.4$ Hz
	$J^{vic}_{CH_3(3)\text{-}CH_2(2)}=7.4$ Hz
	$J^{long}_{CH_3(2)\text{-}CH_2(4)}=1$ Hz

Next, let us examine the spectrum of Sample (IV) by the aid of the spectrum-simulation method. Before doing this, though, we shall preliminarily simulate the spectrum of Sample (V) in order to estimate the vicinal coupling constant. The simulated spectra shown in Figs. 5(c) and 5(d) were obtained by using the "stick" type and the Lorentzian line shape respectively. When the parameters listed in Table 1 are used, the spectrum fairly well fits the observed one except that the calculated methylene part is somewhat sharper than the observed one: this may come from the neglect of the long-range coupling between the $CH_2(2)$ and $CH_2(4)$ protons. Although these parameters are not necessarily the best-fitting ones, they seem to be reasonable. In doing the spectrum simulation of Sample (IV) we

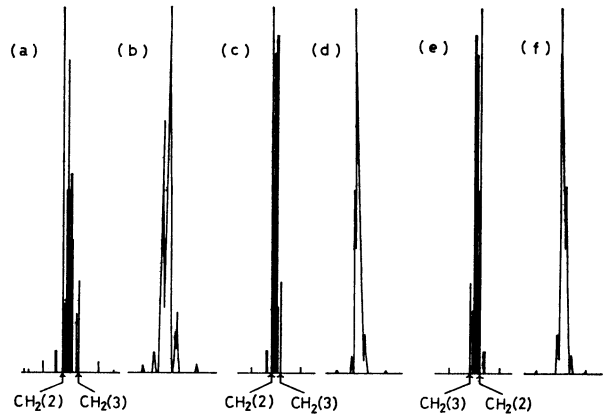

Fig. 6. The calculated spectra of *n*-pentane-1,1,1,5,5,5-d_6 for various values as the chemical shift difference between the $CH_2(3)$ and $CH_2(2)$ protons ($\delta_{CH_2(3)\text{-}CH_2(2)}$).
(a), (c), (e):
Calculated "stick" spectra using the values of 0.05, 0.03, and -0.03 ppm as $\delta_{CH_2(3)\text{-}CH_2(2)}$, respectively. The input chemical shifts of the $CH_2(3)$ and $CH_2(2)$ protons are indicated by the arrow.
(b), (d), (f):
Calculated spectra in Lorentzian line shapes with half-height-width of 0.4 Hz corresponding to (a), (c) and (e), respectively.

will tentatively use the parameters obtained above, that is, the vicinal coupling constant of 7.4 Hz and the long-range coupling of 1 Hz, since we cannot decide the detailed parameters because of the lack of characteristic peaks in Fig. 4(b). These values are, then, approximated such that the coupling constant between the $CH_2(2)$ and $CH_2(3)$ protons is nearly equal to that between the $CH_3(1)$ and $CH_2(2)$ protons: the long-range coupling constant may be somewhat overestimated. Figure 6 shows the calculated spectra of Sample (IV) with the various values for the chemical-shift difference between the $CH_2(2)$ and $CH_2(3)$ protons. As the observed spectrum (Fig. 4(b)) shows a rather sharp shoulder on the lower-field side of the main peak, we shall compare the calculated spectra with the observed one with regard to this shoulder. As is shown in Figs. 6(e) and 6(f), when the chemical shift of the $CH_2(2)$ protons is at a higher field than that of the $CH_2(3)$ protons, the calculated spectrum shows a shoulder on the higher-field side of the main peak: this is in disagreement with the observed spectrum. On the contrary, when the chemical shift of the $CH_2(3)$ protons is at a higher field, the shoulder in the calculated spectrum (Figs. 6(a), (b), (c), and (d)) appears on the lower-field side: this agrees with the observed spectrum. As the difference in chemical shift between the $CH_2(2)$ and $CH_2(3)$ protons becomes large, this shoulder moves away from the center of the main peak and becomes a resolved peak. When the value of 0.03 ppm is used as the chemical shift difference, a better-fitting spectrum seems to be obtained. From the "stick" spectrum (Fig. 6) it is found that the shoulder can be assigned to the $CH_2(2)$ protons, while a weak peak at the foot of the higher-field side, which is hardly shown in the observed spectrum because

of wiggle, can be assigned to the $CH_2(3)$ proton, and that the position of the main peak corresponds to something like the mean value of the chemical shifts between the $CH_2(2)$ and $CH_2(3)$ protons. Thus, we obtained results in accordance with the previous ones[3] by means of the simulation method for Sample (IV) as well as for Samples (II) and (III).

It is well known[4] that the replacement of a hydrogen atom by a deuterium atom causes a small up-field shift in the proton NMR: this is called the isotope shift. We shall examine this effect upon the deuterated *n*-pentanes, since we are concerned with a slight difference in the chemical shift between the methylene protons. The observed isotope shifts of the methyl protons in the deuterated *n*-pentanes are tabulated in Table 2. As has been reported in methane and other molecules by Bernheim *et al.*[5] and Barfield *et al.*[6] it was noted that the magnitude of the isotope shift is proportional to the number of the geminally isotopic substitution. We could not measure the isotope shift of the methylene protons, for we could not decide the exact chemical shifts of the $CH_2(2)$ and $CH_2(3)$ protons in deuterated *n*-pentanes. However, we can expect a very small isotope effect between the $CH_3(1)$ and $CH_2(3)$ groups, because the observed isotope shift of the methyl proton in Sample (V) is very small. Further, if we assume that the isotope effect of the vicinally isotopic substitution is smaller than that of the geminally one, it may not be because of the isotope shift, but because of the difference in the original chemical shift, that the $CH_2(3)$ protons appear at a field higher than the $CH_2(2)$ ones by *ca.* 0.03 ppm in the deuterated *n*-pentanes. Though we could not obtain any information on whether or not the shoulder on the higher-field side of the main peak in the non-deuterated *n*-pentane (Sample (I)) was the signal of the $CH_2(3)$ protons, we obtained experimental results which were in accordance with the theoretically-predicted ones.[3]

TABLE 2. ISOTOPE SHIFTS OF METHYL PROTONS OF *n*-PENTANE IN CCl_4 SOLUTION FOR VARIOUS AMOUNTS OF DEUTERIUM SUBSTITUTION (22.5 °C)

Sample	Isotope shift (ppm)
$CH_3CH_2CH_2CH_2CH_3$	0
$CH_2DCH_2CH_2CH_2CH_2D$	0.016
$CHD_2CH_2CH_2CH_2CHD_2$	0.033
$CH_3CH_2CD_2CH_2CH_3$	0.002

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