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Carbon-13 NMR Chemical Shift and Electronic Structure of Solid Polypeptides as Studied by Tight-binding MO Theory. Polyglycine and Poly(L-alanine)

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A tight-binding MO-sum-over-state theory has been used to calculate the ^{13}C NMR chemical shift of polyglycine having the forms I and II and that of poly(L-alanine) having the α-helix and β-sheet forms, in order to justify the origin of the conformation-dependent ^{13}C NMR chemical shift previously determined by the cross polarization-magic angle spinning technique. The calculated results on the carbonyl, C_α and C_β carbons were found to exhibit the conformation-dependent ^{13}C NMR chemical shifts comparable with the experimental data.

A recent development of the cross polarization-magic angle spinning (CP–MAS) NMR technique has provided useful information about the conformation of polypeptides in the solid state.[1–12] It has been demonstrated that the ^{13}C chemical shifts of the C_α, C_β, and carbonyl carbons are displaced up to 7 ppm, depending on the particular conformations such as the α-helix, β-sheet and ω-helix forms.

In a previous work,[7] we have justified by using a dipeptide fragment of poly(L-alanine), *N*-acetylalanine methylamide, and the finite perturbation theory(FPT) within the INDO MO framework[13–17] that the conformation-dependent ^{13}C chemical shift arises from changes of electronic structure varying with the dihedral angles (ϕ and ψ) of the skeletal bond. (On the other hand, Tonelli[33] has suggested that ^{13}C NMR chemical shifts of backbone carbonyl and side chain carbons in polypeptides provide information about their structure by means of the γ-gauche effect.) Such approaches are useful to obtain appropriate knowledge regarding the conformation of polypeptides. However, it may be necessary to clarify the following points: The specification of the long finite interaction length for the electronic structure, and the hydrogen bond's involved in the α-helix or β-sheet form are not always included sufficiently in the dipeptide.

Such a situation leads to the application of the tight-binding (TB) MO theory to the NMR chemical shift calculation for polypeptides without using the model compounds.[18] It is emphasized that the intrachain hydrogen bonds of the α-helix conformation are easily taken into account by this approximation. So far, the TB MO approximation has been used for describing the electronic structure of polymers with a periodic structure.[19–25] Thus, in this work we attempt to calculate the conformation-dependent ^{13}C chemical shift for polyglycine and poly(L-alanine) which was previously measured, on the basis of the TB MO approximation in order to gain an insight into the ^{13}C chemical shift in polypeptides.

Theory and Calculation

With the aid of the LCAO approximation and Bloch's theorem, the wave function for electrons in a polymer chain in which N-1 cells (or amino acid residues) interact with the original cell is expressed by[19–21]

$$\Psi_n(k,r) = \frac{1}{N}\sum_{\nu}\sum_{j}\exp(ikj)C_{\nu n}(k)\phi_\nu(r-ja), \tag{1}$$

where n is the band index; ν the atomic orbital in the j-th cell; N the total number of cells; 1 the number of atomic orbital in the cell; a the unit vector of translational symmetry and k the wave number. The parameters j and k vary from $-(N-1)/2$ to $(N-1)/2$ and from $-\pi/2$ to $\pi/2$, respectively, within the first Brillouin zone. The symbol i denotes the imaginary number. $\phi_p(r-ja)$ represents the p-th atomic orbital in the j-th cell and $C_{\nu n}(k)$ its expansion coefficient. Using Eq. 1, the Schrödinger equation for a polymer chain is given by

$$H(k) = \varepsilon(k)S(k), \tag{2}$$

where

$$\begin{aligned} H_{\mu\nu}(k) &= \sum_j \exp(ikj)H^{0j}_{\mu\nu}, \\ S_{\mu\nu}(k) &= \sum_j \exp(ikj)S^{0j}_{\mu\nu}, \end{aligned} \tag{3}$$

in which $H^{0j}_{\mu\nu}$ is the interaction between the μ-th atomic orbital in the original cell and the ν-th atomic orbital in the j-th cell. $S^{0j}_{\mu\nu}$ is the overlap integral between the μ-th atomic orbital in the original cell and the ν-th atomic orbital in the j-th cell. Thus, we can directly treat a polymer chain which has infinite length without model compounds such as a dimer, trimer, *etc.* Previously, the electronic structure of polymers (including polyglycine and poly(L-alanine)) were calculated by means of the extended Hückel and CNDO MO theories and conformational energies were compared.[22–25]

Hence, we perform calculations within the framework of the extended Hückel approximation. It is said that the extended Hückel calculation should be compared among molecules with a similar structure, because, generally, such a calculation for polar molecules has a tendency to overestimate the electronic polarization. Therefore, it is considered that the extended Hückel method is significantly applicable to the conformation-dependent ^{13}C chemical shift calculation as done in this work. In the extended Hückel approximation, the diagonal and off-diagonal elements of the Hamiltonian are estimated as follows:

$$\begin{aligned} H^{00}_{\mu\mu} &= -I_\mu \\ H^{0j}_{\mu\nu} &= \frac{1}{2}KS^{0j}_{\mu\nu}(H^{00}_{\mu\mu}+H^{00}_{\nu\nu}), \end{aligned} \tag{4}$$

where I_μ is the ionization potential energy of the μ-th orbital and K is taken to be 1.75. The valence-state ionization potential energy for the paticular atomic orbital used here is as follows:[26] I_{1s}=13.6 eV for hydrogen atom; I_{2s}=21.43 eV and I_{2p}=11.42 eV for carbon atom; I_{2s}=27.5 eV and I_{2p}=14.49 eV for nitrogen atom; I_{2s}=35.3 eV and I_{2p}=17.76 eV for oxygen atom. The Slater's effective nuclear charges used for hydrogen, carbon, nitrogen and oxygen atoms are 1.00, 3.25, 3.90, and 4.55, respectively.[26] Thus, we can directly obtain the expansion coefficients, $C_{\nu n}(k)$, and the electronic structure of an infinite regular polymer.

Using $C_{\nu n}(k)$, we estimate the ^{13}C NMR chemical shift of polyglycine and poly(L-alanine). In general, an NMR chemical shift can be written as

$$\sigma_A = \sigma^d_A + \sigma^p_A + \sigma', \tag{5}$$

where σ^d_A and σ^p_A are the diamagnetic and paramagnetic contributions, respectively. σ' is the contribution from neighbouring atoms. For the carbon atom, σ' is much smaller than 1 ppm and can be considered negligible. Thus, the ^{13}C NMR chemical shift can be estimated by the sum of σ^d and σ^p which are expressed by[18]

$$\sigma^d_A(k) = \frac{\mu_0}{4\pi}\frac{2e^2}{3m_e^2}\sum_{\nu}^{A}\sum_{\nu'}^{A} P_{\nu\nu'}(k)\langle\phi_\nu(r)|r^{-1}|\phi_{\nu'}(r)\rangle \tag{6}$$

$$\begin{aligned} \sigma^p_{A,\alpha\beta}(k) = -\frac{\mu_0}{4\pi}\frac{\hbar^2e^2}{m_e^2}\sum_{m}^{occ}\sum_{n}^{unocc}\sum_{j}^{A}\langle r^{-3}\rangle_{2p}({}^1E^n_m-{}^1E_0)^{-1} \\ \times \sum_{B}^{B}\sum_{l} (X(j,m,n,\beta,\gamma)X(l,n,m,\gamma,\alpha) \\ - Y(j,m,n,\beta,\gamma)Y(l,n,m,\gamma,\alpha) \\ + X(j,m,n,\gamma,\alpha)X(l,n,m,\beta,\gamma) \\ - Y(j,m,n,\gamma,\alpha)Y(l,n,m,\beta,\gamma)), \end{aligned} \tag{7}$$

where

$$\begin{aligned} P_{\nu\nu'}(k) &= \sum_{m}^{occ} C^*_{\nu n}(k)C_{\nu' m}(k) \\ X(j,m,n,\beta,\gamma) &= C^{R\beta}_{jm}C^{I\gamma}_{jn} + C^{R\beta}_{jn}C^{I\gamma}_{jm} - C^{R\gamma}_{jn}C^{I\beta}_{jm} - C^{R\gamma}_{jm}C^{I\beta}_{jn} \\ Y(j,m,n,\beta,\gamma) &= C^{R\beta}_{jm}C^{R\gamma}_{jn} - C^{R\gamma}_{jm}C^{R\beta}_{jn} + C^{I\beta}_{jm}C^{I\gamma}_{jn} - C^{I\gamma}_{jm}C^{I\beta}_{jn} \end{aligned} \tag{8}$$

in which j and l are orbitals on atoms A and B, respectively; $\sum\limits_{m}^{occ}$ and $\sum\limits_{n}^{unocc}$ are the summations over the occupied and unoccupied orbitals, respectively; α, β, γ=x, y, z in cyclic order; and R and I represent the real and imaginary parts of coefficient $C_{\nu n}(k)$, respectively.

The geometry data on polyglycine and poly(L-alanine) obtained from an X-ray diffraction analysis are used, and the dihedral angles (ϕ and ψ) are listed in Table 1. The structure of the hydrogen-bonded two polypeptide chains is shown in Fig. 1. The calculation for the two chains is carried out as a function of the hydrogen-bond length, R.

In the tight-binding MO calculation, it is important to determine the number of divisions for the wave vector, k. In a previous paper[18] on the ^{13}C chemical shift for polyethylene, we obtained the results that the ^{13}C chemical shift of polyethylene converges to a definite value as the number of the divisions increases. The magnitude of the variation of ^{13}C chemical shift is smaller than 0.1 ppm if the number of divisions exceeds 20. For this reason, we chose 60 and 30 points as the number of divisions for polyglycine and poly(L-alanine), respectively.

The calculations were performed on a HITAC M200H computer in the Computer Center of Tokyo Institute of Technology and a HITAC M200H computer in the Computer Center of Institute for Molecular Science, Okazaki.

Results and Discussion

Polyglycine. First, we are dealing with an isolated polymer chain. In Table 2 are shown the calculated and observed ^{13}C chemical shifts of a polyglycine chain with forms I and II. The calculated chemical

Table 1. The dihedral angle used in the TB MO calculation for polyglycine and poly(L-alanine)

	Dihedral angle (degree)	
	ϕ	ψ
Polyglycine[a)]		
form I	−142.0	145.0
form II	−76.0	146.0
Poly(L-alanine)[b)]		
α_R-helix	−66.8	−43.7
α_L-helix	66.8	43.7
β-sheet	−138.6	134.7

a) Refs. 27 and 28. b) α_R- and α_L-helix forms indicate the right-handed and left-handed β-helix forms, respectively. (Ref. 29).

Table 2. The observed and the calculated ^{13}C chemical shifts of an isolated polyglycine chain (in ppm)

	$\delta^{a)}_{obsd}$		$\sigma^{b)}_{calcd}$	
	form I	form II	form I	form II
CH_2	43.5	43.5	−127.2	−124.4
C=O	168.4	172.3	−236.7	−248.1

a) From TMS. The positive sign means deshielding. (Refs. 5 and 12). b) The negative sign means deshielding.

shift (σ) is a nuclear shielding constant and so the negative sign means deshielding. On the other hand, the negative sign of the observed chemical shift means shielding. Therefore, the relative difference in the calculated chemical shift (σ) should be compared with the observed chemical shifts (δ). The observed carbonyl ^{13}C chemical shift for form I appears at higher field by about 4 ppm than that for form II. The calculated ^{13}C chemical shift for form I appears at higher field by about 11 ppm than that in form II, which is in parallel with the experimental finding. There is no significant difference between the methylene ^{13}C chemical shifts for forms I and II within the experimental error. In this stage, we cannot determine whether the chemical shift for form I or II appears at higher field. On the other hand, the calculated ^{13}C chemical shift for form I appears at lower field by about 3 ppm than that for form II, so the calculation predicts the existence of a chemical shift difference (about 3 ppm) between forms I and II. It appears that the calculated shifts are somewhat exaggerated as compared with the observed values. Nevertheless, the observed trend that the ^{13}C chemical shift difference for the methylene carbon is considerably small compared with that for the carbonyl carbon, is reproduced qualitatively by the calculation. Accordingly, the overall trend in the observed conformation-dependent ^{13}C chemical shift of polyglycine can be qualitatively explained by the present calculation.[34)]

Up to now we have dealt with an isolated polymer chain. However, real polymer chains in the solid state interact with each other. Especially, polyglycine has the hydrogen bond in both of forms I and II.[29,30)] Form I has an antiparallel β-sheet structure and each chain has a hydrogen bond with both sides of the chains in the sheet. Form II has 3_1-helix structure and each chain is intermolecularly hydrogen-bonded to six surrounding chains. Therefore, it is important to investigate the effect of the hydrogen bond on the ^{13}C chemical shift. Then, we carried out a TB MO calculation on the ^{13}C chemical shift of polyglycine for forms I and II considering the effect of the hydrogen bond. In the TB MO

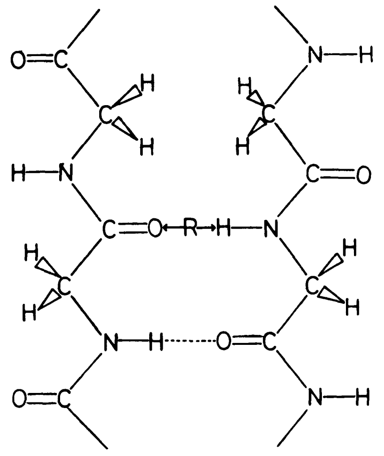

Fig. 1. The structure of two hydrogen-bonded β-sheet chains. R is the distance between oxygen and hydrogen atoms.

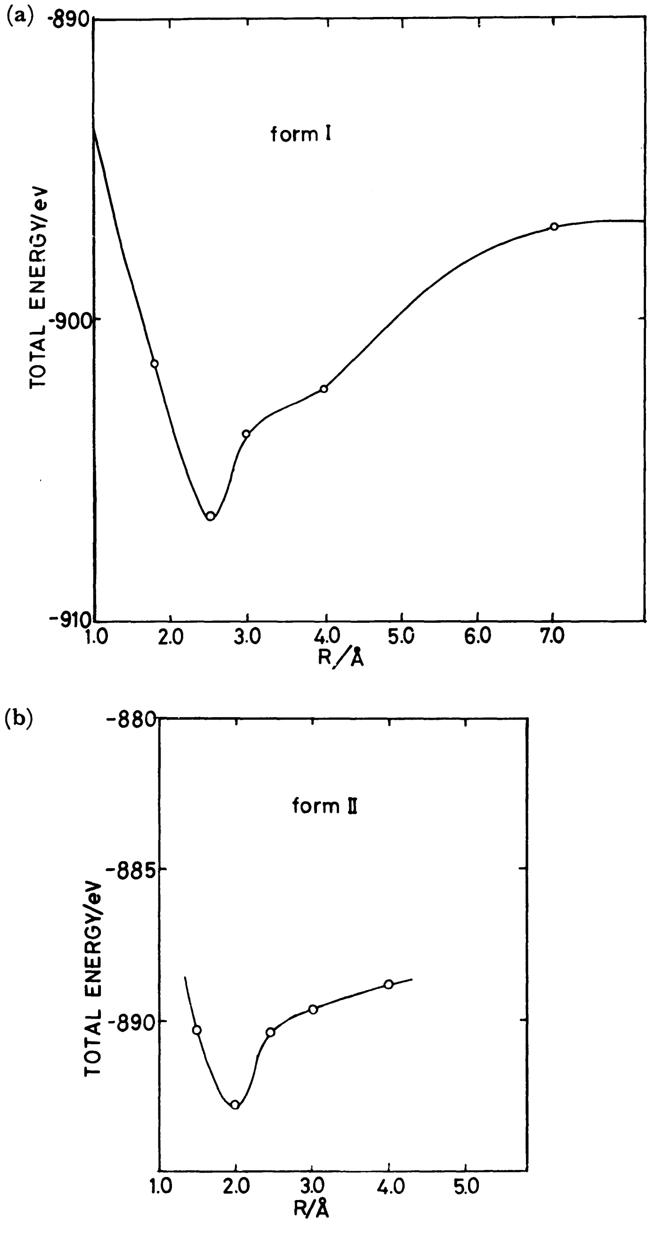

Fig. 2. The R dependence of the total electronic energy of polyglycine.
(a): form I, (b): form II.

calculation, it is not practical in this stage to treat the complete molecular structure of polyglycine in the solid state, which was determined from X-ray diffraction, because the TB MO calculation requires a very long calculation time and a large memory in the computer. Thus, instead of a real molecular structure, we will treat the two polyglycine chains which are hydrogen-bonded to each other (Fig. 1). In Fig. 1, R stands for the distance between the oxygen atom and the hydrogen atom bonded to the nitrogen atom. The TB MO calculation on the ^{13}C chemical shift was carried out as a function of R, in order to evaluate the influence of the hydrogen bond on the chemical shift. The calculation on form II was carried out in a similar manner. In Figs. 2 (a) and (b) is shown the R dependence of the total electronic energy of polyglycine in forms I and II, respectively. Obviously, form I has the energy minimum at about 2.5 A, and form II at 2.0 A. In the former the distance between the nitrogen and the oxygen atoms involved in the hydrogen bond for form I is longer than that for form II. It is known from an X-ray diffraction study that the distances between the nitrogen and oxygen atoms in forms I and II are 2.95 and 2.73 A, respectively.[30,31] Taking into account that the length of the N-H bond is 1.0 A, the above-calculated results are in parallel with the results found by X-ray diffraction: The length in form I is longer than that in form II.

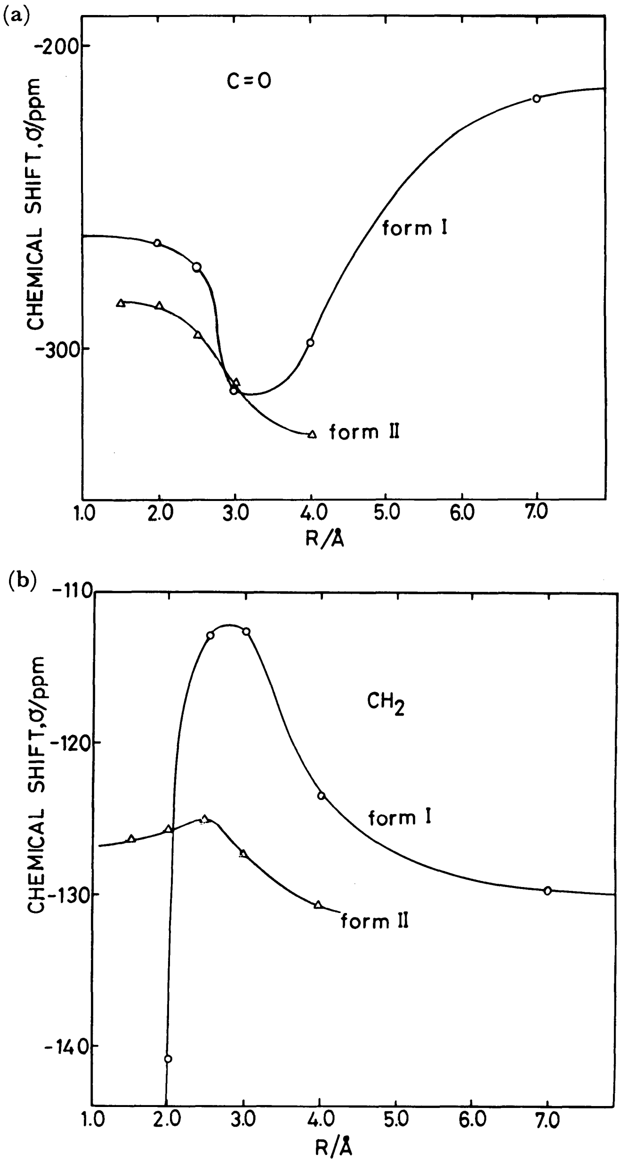

Fig. 3. The R dependence of the calculated ^{13}C NMR chemical shift of the carbonyl carbon (a) and methylene carbon (b) in polyglycine.
○: form I, △: form II.

Next, we will discuss the R dependence of the ^{13}C chemical shift for forms I and II. In Fig. 3(a) is shown the R dependence of the ^{13}C chemical shift of the carbonyl carbons for forms I and II. In the case of form I, for the carbonyl ^{13}C chemical shift moves downfield as R increases from 2 to 3.2 A, and upfield as R increases further from 3.2 A. In the case of form II, the carbonyl ^{13}C chemical shift moves downfield as R increases. Comparing this with the results for an isolated polymer chain, the carbonyl ^{13}C chemical shifts for both forms I and II appear largely downfield. This means that the carbonyl ^{13}C chemical shift moves largely downfield caused by the hydrogen bonding. At the minimum energy position (R=2.5 and 2.0 A for forms I and II, respectively), the carbonyl ^{13}C chemical shift for forms I and II are −274.9 and −286.2 ppm, respectively (Figs. 2 and 3). Thus, the carbonyl ^{13}C chemical shift for form I appears upperfield than that for form II, again consistent with the experimental finding. In Fig. 3(b) is shown the R dependence of the methylene ^{13}C chemical shift. The R dependence of the ^{13}C chemical shift of the methylene carbon is much smaller than that of the carbonyl carbon. Especially, the R dependence of the methylene ^{13}C chemical shift for form II is very small. This may be due to a fact that the carbonyl carbon is directly involved in the hydrogen bond, but the methylene carbon is not. In the case of form I, the methylene ^{13}C chemical shift moves to upfield, as R increases from 2 to 2.8 A, and to downfield as R increases further from 2.8 A. In the case of form II, the ^{13}C chemical shift is similar to that of form I, but the magnitude of the change is much smaller compared with that for form I. At the minimum energy position the ^{13}C chemical shift of the methylene carbon for forms I and II are −112.9 and −126.0 ppm, respectively. Therefore it appears that the difference in ^{13}C chemical shift of the methylene carbon between forms I and II is much overemphasized. Experimentally, the ^{13}C chemical shift of the methylene carbon for form I is almost the same as that in form II. The ^{13}C chemical shift of the methylene carbon for form I changes largely in the vicinity of the energy minimum position, especially in the range of R between at 2.0

and 2.5 A. Therefore, this shows that the electronic structure of form I changes considerably in this region. As shown in Fig. 3(b), the ^{13}C chemical shift of the methylene carbon for form I moves to downfield as R decreases from the value at the energy minimum, and at the value of about 2.3 A it becomes almost equal to the ^{13}C chemical shift of the methylene carbon in form II. At this value of R, the ^{13}C chemical shift of the carbonyl carbon for form I appear at higher field than that for form II, and this result coincides with the observation. It is plausible that the R value obtained by the energy minimization of the two chains might be slightly modified by taking into account many chains in the solid state. Thus, by considering the hydrogen bond, we can reasonably explain the behavior of the ^{13}C chemical shift for forms I and II.

Poly(L-alanine) In Table 3 are shown the calculated and observed ^{13}C chemical shifts of poly(L-alanine). First, we consider the ^{13}C chemical shift of poly(L-alanine) taking the α-helix form. It is known that poly(L-alanine) has an right-handed α-helix(α_R-helix) form, but that the L-alanine residues are incorporated into the left-handed α-helix (α_L-helix) in D-alanine sequence in the random copolymers consisting of L- and D-alanines.[23] Therefore, we consider the ^{13}C chemical shifts of poly(L-alanine) in the α_R- and α_L-helix forms. We have already reported that the observed C_α and carbonyl ^{13}C chemical shifts of L-alanine residues incorporated into the α_L-helix form in the D-alanine sequence are between those in the β-sheet and α_R-forms and appears near that in the β-sheet form, while the C_β shift of the α_L-helix is close to that of the α_R-helix.[3,7] As seen from Table 3, the calculated ^{13}C chemical shifts of the C_α, C_β, and carbonyl carbons move to upfield (6.7 ppm), downfield (−1.3 ppm) and upfield(10.3 ppm), respectively, when the conformation changes from the α_R-helix to α_L-helix form. Experimentally, displacements of signals are 3.3, 0.0, 3.5, ppm for C_α, C_β, and carbonyl carbons, respectively. Therefore, the present calculation reproduces the experimental data.[34]

Next, we discuss the ^{13}C chemical shift for the β-sheet form. In the above calculation of α_R- and α_L-helix forms, we were able to include the O(=C) and H(−N) atoms making hydrogen bond without any difficulty. In the β-sheet form, where the hydrogen bonds are formed between chains, we calculated the ^{13}C chemical shift for the β-sheet form by taking into account the hydrogen bonds as a similar manner as that of polyglycine (Fig. 1). In Fig. 4 is shown the R dependence of the total electronic energy of poly(L-alanine). As seen from this figure, the energy minimum exists at R=2.75 A. From the results of an X-ray diffraction study, it is known that the distance between the nitrogen and oxygen atoms in the β-sheet form is 2.83 A.[29] If the distance between the nitrogen and hydrogen atoms is about 1.0 A, the distance between the oxygen and hydrogen atoms determined from the X-ray diffraction study is 1.83 A. The calculated results are longer than those from the X-ray diffraction, as also encountered in the calculation of forms I and II of polyglycine taking into account intermolecular hydrogen bonds. This may be due to the fact that the extended Hückel MO method is often apt to overestimate the polarity of a molecule. In Figs. 5 (a), (b), and (c) are shown the R dependences of the ^{13}C chemical shift of the C_α, C_β, and carbonyl carbons, respectively. It is shown that the ^{13}C chemical shifts of the C_α and C_β carbons moves to upfield from 2.0 to 3.6 A and downfield further from 3.6 A as R increases. On the other hand, in the case of the carbonyl carbon, the ^{13}C chemical shift moves to downfield from 2 to 3.7 A and then upfield above 3.7 A as R increases. The carbonyl carbon shows the largest R-dependence. This result agrees with the result for polyglycine. The carbonyl carbon is bonded directly to the oxygen atom by a double bond and a transfer of electrons from the carbon to the more electronegative oxygen occurs. At the energy minimum (R=2.75 A), the ^{13}C chemical shifts of the C_α, C_β, and carbonyl carbon are −144.5, −99.3, and −287.0 ppm, respectively, as seen from Fig. 5. These values of the C_α, C_β, and carbonyl carbon for the β-sheet form appear upperfield (7.0 ppm), lowerfield

TABLE 3. THE OBSERVED AND THE CALCULATED ^{13}C CHEMICAL SHIFTS OF AN ISOLATED POLY(L-ALANINE) CHAIN (in ppm)

	$\delta^{a)}_{obsd}$			$\sigma^{b)}_{calcd}$		
	α_R	α_L	β	α_R	α_L	β
$CH_3(C_\beta)$	14.9	14.9	19.9	−94.8	−96.1	−98.3
$CH(C_\alpha)$	52.4	49.1	48.2	−151.5	−144.8	−143.0
C=O	176.4	172.9	171.8	−278.1	−267.8	−245.8

a) From TMS. The positive sign means deshielding. (Refs. 3 and 7). b) The negative sign means deshielding.

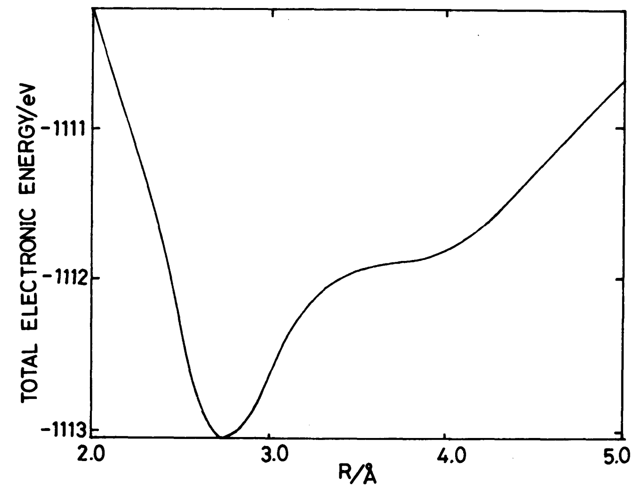

Fig. 4. The R dependence of the total electronic energy of poly(L-alanine) in the β-sheet form.

(−4.5 ppm) and lowerfield (−8.9 ppm), respectively as compared with the shielding values of the α_R-helix form (Table 3). Experimentally, however, the ^{13}C NMR chemical shifts of the C_α, C_β, and carbonyl carbon for the β-sheet form appear upperfield (4.2 ppm), lowerfield (−5.0 ppm) and upperfield (4.6 ppm), respectively, compared with those for the α_R-helix. Therefore, it is shown that the calculated shielding constant for the carbonyl carbon at the minimum energy is not consistent with the experimental results, although the C_α and C_β chemical shifts are well reproduced. This is caused by that the carbonyl ^{13}C chemical shift is extremely sensitive to the hydrogen bond distance R. Another possibility is that the R value determined by the energy minimum should be slightly modified when many chains more than two chains are hydrogen-bonding in the real β-sheet form. Therefore, it is worthwhile to examine the "R" value which reproduces the experimental data instead of the R value at the energy minimum. For this, the ^{13}C chemical shift value for the α_R-form is indicated by the dashed line in Fig. 5. (The solid line indicates the ^{13}C chemical shift for the β-sheet form.) For the C_α, C_β, and carbonyl carbons both the lines intersect with each other at R=2.5 A, 3.0 A, and 2.56 A, respectively. Accordingly, the approximate value of R at which the calculated results are in parallel with the experimental result falls on the range of 2.5 to 2.56 A. This range is still longer than the length for the hydrogen bond determined from X-ray diffraction. Such an argument, however, arose from the use of an inadequate wavefunction such as the extended Hückel MO approximation. It is probable that this sort of problem might easily be resolved when more accurate wavefunctions such as CNDO, INDO or non-empirical theory are employed.

Nevertheless, the present calculation is very useful because the conformation-dependent ^{13}C chemical shifts in polypeptides are reproduced with some limitation. A more refined calculation using the tight-binding CNDO MO is in progress.

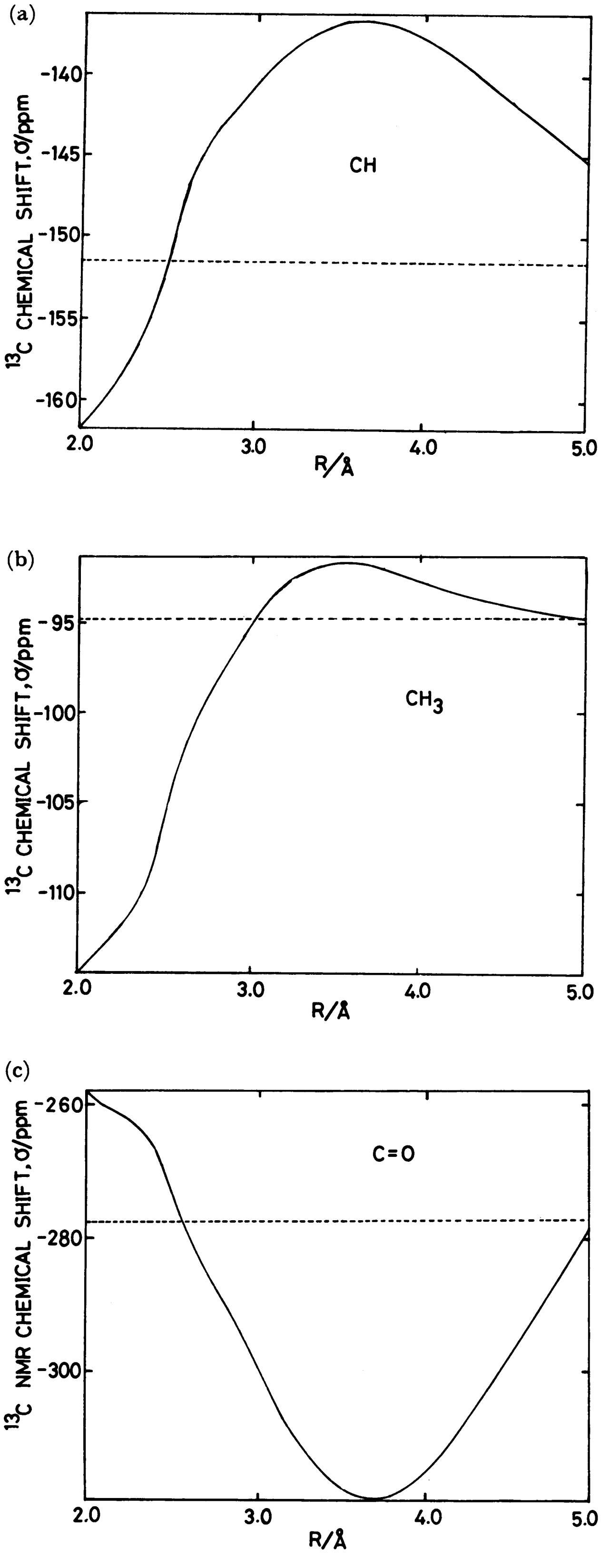

Fig. 5. The R dependence of the calculated ^{13}C NMR chemical shift of poly (L-alanine) in the β-sheet. The solid line is for two hydrogen-bonded β-sheet chains. The dashed line indicates the ^{13}C chemical shift value for an isolated α-helix chain.
(a): C_α, (b): C_β, (c): C=O.

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34) In some conjugated aromatic compounds, it is known that there is the close relationship between the ^{13}C chemical shift and electron density on the carbon atom. However, it was found that the relationship between the conformation-dependent ^{13}C chemical shift and electron density on the C_α, C_β, and carbonyl carbon atoms does not exist.