was used for the ^{13}C and ^{2}D spectra; these were recorded after carefully eliminating drift.

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Calculation of Chemical Shifts of Inner-Shell Electrons for the DNA Bases by the CNDO/2 Method Including the Charge Redistribution Effect

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Abstract: A simple treatment for the calculation of the chemical shift including the charge redistribution effect was developed by using the CNDO/2 molecular orbital method. This formalism was applied to the chemical shifts of the carbon and the nitrogen atoms in the DNA base components. For the carbon atoms, the chemical shifts were found to correlate excellently with the calculated binding energies which were obtained by the CNDO/2 method without modification of the parameters included in the method. The net charges on the carbon atoms also correspond fairly well with their chemical shifts. For the nitrogen atoms, the change of the parameters which corresponds to take the change of the core potential into account leads to a good agreement between the calculated and the observed chemical shifts. These situations were rationalized from the charge distributions of the molecules before and after the ionization of an inner-shell electron.

The finding of the chemical shift in the binding energy of the inner-shell electron has made it possible to use this method, called ESCA,[1,2] as a powerful tool for the analysis of the molecular structure of organic as well as inorganic molecules. The chemical shifts thus measured have been found to correlate intimately with the charge distribution of valence-shell electrons. Many calculations of the chemical shift have been carried out by using various molecular orbital methods, that is, the iterative extended Hückel method,[3] the CNDO method,[4] and *ab initio* calculations.[5–10] It has been shown that the charge on the atom in question could be related to its chemical shift,[3,4] but *Gelius, et al.*,[11] have indicated that the chemical shift depends not only on the charge on the ionized atom but also on the charge on the other atoms. Further, Kato, *et al.*,[12] have derived the dependency of the chemical shift on the charges of many atoms, by taking the localizing character of the inner-shell electrons into account. They applied their formalism to carbon and nitrogen atoms of many organic as well as inorganic molecules using the charges evaluated by the CNDO/2 method. A similar but somewhat different treatment has also been proposed by Ellison and Larcom.[13] In addition to this, the recent studies indicated that the charge redistribution occurs upon the ionization of an inner-shell electron and the contribution of the redistribution to the chemical shift was found not to be negligible.[12,14–16] In these researches relatively simple molecules were treated since the *ab initio* calculation for large molecules in ionized states is tremendous.

In the present paper, a relatively simple treatment of the chemical shift is developed by using the CNDO/2 method,[17–19] including the charge redistribution effect. That is, when the inner-shell electron on an atom was ionized, the valence electron is considered to feel the core potential different from that in the neutral molecule. Since all the valence electrons occupy the closed-shell orbitals before and after ionization and the chemical shift is primarily due to valence-shell electrons, the total energies of both neutral and ionized molecules can be calculated by the usual semiempirical closed-shell SCF method, that is, the CNDO/2 method. The only difference in the treatment between neutral and ionized molecules is the usage of different values for the parameters in the CNDO/2 method, which reflect the change of the core potential caused by the ionization. The treatment, details of which will be given in the following chapter, was applied to the chemical shifts of

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the carbon and the nitrogen atoms in the DNA bases since these molecules are not only biologically important but also of special interest from the electronical structural point of view. These bases have some carbon and nitrogen atoms in electronically slightly different circumstances and, hence, are appropriate to the theoretical study of the chemical shifts. Barber and Clark measured the chemical shifts of some of the DNA bases, that is, adenine, thymine, and cytosine,[20] and they assigned the experimental binding energies to specific atoms by comparing their experimental data with the 1s orbital energies calculated by means of the *ab initio* molecular orbital method.[21] Thus the assignment is not unambiguous. However, the linear relations between the calculated and the observed binding energies were found intramolecularly, and, hence, the assignments may most likely be correct. On the other hand, the linear relation between the theoretical values and the experimental values was not obtained intermolecularly. Recently, Ishida, *et al.*,[22] also calculated the chemical shifts of the carbon and the nitrogen atoms in the DNA bases to find excellent correlation for the carbon atoms but less for the nitrogen atoms. Under these circumstances, the treatment in the present paper was applied to the DNA bases to clarify the reason of discrepancy between theoretical and experimental values of chemical shifts for the nitrogen atoms.

Method of Calculation

The wave function for neutral molecules was represented as a single determinant, namely

$$\Psi = |\varphi_1(1)\bar{\varphi}_1(2), \ldots, \varphi_n(2n - 1)\bar{\varphi}_n(2n)\chi_1(2n + 1)\bar{\chi}_1(2n + 2), \ldots, \chi_m(2n + 2m - 1)\bar{\chi}_m(2n + 2m)| \quad (1)$$

where φ_i, $\bar{\varphi}_i$ are the molecular orbitals for valence shell electrons with α spin and β spin, respectively, and where χ_k, $\bar{\chi}_k$ are those for inner-shell electrons. The orbitals for inner-shell electrons, χ_k's, were assumed to localize on the corresponding atom, while the orbitals for valence electrons, φ_i's, are spread out over the whole molecule. This assumption on the localizability of the inner-shell orbitals can be rationalized by the molecular orbitals calculated nonempirically; the *ab initio* calculations with Gaussian basis sets have indicated that inner-shell atomic orbitals are localized on the particular atoms.[21] The same assumption had already been used to obtain the relation between charge distributions of molecules and chemical shifts of inner-shell electrons by Kato, *et al.*[12,22] In order to distinguish between the inner-shell and the valence-shell orbitals in the present paper, *k* and *l* were used to represent the inner-shell orbitals, *i* and *j* the valence-shell orbitals, and *t* the ionized inner-shell orbital. In addition to the assumption of the localizability of inner-shell orbitals, all the molecular orbitals including inner-shell orbitals are supposed to be orthogonal to each other throughout this paper.

The total electronic energy for a neutral molecule is given by using eq 1

$$E = 2\sum_{i=1}^{n}(i|h|i) + 2\sum_{k=1}^{m}(k|h|k) + \sum_{i=1}^{n}\sum_{j=1}^{n}\{2(ii|jj) - (ij|ij)\} + 2\sum_{i=1}^{n}\sum_{k=1}^{m}\{2(ii|kk) - (ik|ik)\} + \sum_{k=1}^{m}\sum_{l=1}^{m}\{2(kk|ll) - (kl|kl)\} \quad (2)$$

where

$$(i|h|i) = \int \varphi_i^*\left(-{}^1\!/_2\Delta + \sum_A Z_A/R_A\right)\varphi_i \mathrm{d}\tau \quad (3)$$

$$(ii|jj) = \int\int \varphi_i^*(1)\varphi_j^*(2)1/R_{12}\varphi_i(1)\varphi_j(2)\mathrm{d}\tau_1\mathrm{d}\tau_2 \quad (4)$$

and so on. The summation with the suffix *A* in eq 3 means that all the atoms in the molecule are summed up.

The wave function for an ionized molecule is

$$\Psi^+ = |\varphi_1{}^+(1)\bar{\varphi}_1{}^+(2), \ldots, \varphi_n{}^+(2n - 1)\bar{\varphi}_n{}^+(2n), \chi_1{}^+(2n + 1)\bar{\chi}_1{}^+(2n + 2), \ldots, \chi_{t-1}{}^+(2n + 2t - 3)\bar{\chi}_{t-1}{}^+(2n + 2t - 2), \chi_t{}^+(2n + 2t - 1)\chi_{t+1}{}^+(2n + 2t)\bar{\chi}_{t+1}{}^+(2n + 2t + 1), \ldots, \chi_m{}^+(2n + 2m - 2)\bar{\chi}_m{}^+(2n + 2m - 1) \quad (5)$$

where the superscript + means that molecular orbitals for an ionized molecule are different from those for the same neutral molecule. Accordingly, the total electronic energy for the ionized molecule contains the electron redistribution energy due to the ionization of an inner electron, which is usually known not to be negligible. In eq 5, an inner electron in the inner-shell atomic orbital, χ_t, was ionized. The total electronic energy for the ionized molecule is

$$E^+ = 2\sum_{i=1}^{n}(i^+|h|i^+) + 2\sum_{k=1}^{m}(k^+|h|k^+) - (t^+|h|t^+) + \sum_{i=1}^{n}\sum_{j=1}^{n}\{2(i^+i^+|j^+j^+) - (i^+j^+|i^+j^+)\} + 2\sum_{i=1}^{n}\sum_{k=1}^{m}\{2(i^+i^+|k^+k^+) - (i^+k^+|i^+k^+)\} + \sum_{k=1}^{m}\sum_{l=1}^{m}\{2(k^+k^+|l^+l^+) - (k^+l^+|k^+l^+)\} - \sum_{i=1}^{n}\{2(i^+i^+|t^+t^+) - (i^+t^+|i^+t^+)\} - \sum_{k=1}^{m}\{2(k^+k^+|t^+t^+) - (k^+t^+|k^+t^+)\} \quad (6)$$

The difference between the total energy for the ionized molecule and that for the neutral molecule is the binding energy of the inner-shell electron which is

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given in eq 7. When $\varphi_i^+ = \varphi_i$ and $\chi_k^+ = \chi_k$, that is,

$$
\begin{aligned}
I_p = E^+ - E = \\
& 2\sum_{k=1}^{m}\{(k^+|h|k^+) - (k|h|k)\} - (t^+|h|t^+) + \\
& \sum_{k=1}^{m}\sum_{l=1}^{m}\{2(k^+k^+|l^+l^+) - (k^+l^+|k^+l^+) - \\
& 2(kk|ll) + (kl|kl)\} + \Bigg[2\sum_{i=1}^{n}(i^+|h|i^+) + \\
& 2\sum_{i=1}^{n}\sum_{k=1}^{m}\{2(i^+i^+|k^+k^+) - (i^+k^+|i^+k^+)\} + \\
& \sum_{i=1}^{n}\sum_{j=1}^{n}\{2(i^+i^+|j^+j^+) - (i^+j^+|i^+j^+)\} - \\
& \sum_{i=1}^{n}\{2(i^+i^+|t^+t^+) - (i^+t^+|i^+t^+)\}\Bigg] - \\
& \Bigg[2\sum_{i=1}^{n}(i|h|i) + 2\sum_{i=1}^{n}\sum_{k=1}^{m}\{2(ii|kk) - \\
& (ik|ik)\} + \sum_{i=1}^{n}\sum_{j=1}^{n}\{2(ii|jj) - (ij|ij)\}\Bigg] - \\
& \sum_{k=1}^{m}\{2(k^+k^+|t^+t^+) - (k^+t^+|k^+t^+)\} \qquad (7)
\end{aligned}
$$

the redistribution effect is neglected, the ionization energy by eq 7 becomes equal to that given by the Koopman theorem, *i.e.*, the orbital energy.

Since the calculation of the binding energy of an inner-shell electron by eq 7 is tremendous, a few approximations are used in order that the calculation of the inner-shell binding energy becomes tractable, as shown below.

(i) When k is not equal to t, χ_k^+ is assumed to be the same as χ_k.

(ii) The two-center Coulomb repulsion integrals between inner-shell electrons are approximated by

$$(kk|t^+t^+) = (kk|tt) = 1/R_{tk} \qquad (k \neq t) \qquad (8)$$

where R_{tk} is the distance between atoms t and k. This approximation is expected to be reasonable because of the localizability of the inner-shell orbital.

(iii) The electron-nucleus attraction integrals for the inner-shell electrons are approximated by

$$(tt|Z_k/R_k) = (t^+t^+|Z_k/R_k) = Z_k/R_{kt} \qquad (9)$$

where

$$(tt|Z_k/R_k) = \int \chi_t^*(1)\chi_t(1)Z_k/R_{1k}\mathrm{d}\tau \qquad (10)$$

and so on.

(iv) The molecular orbitals for valence shell electrons are represented by the linear combination of the valence-shell atomic orbitals

$$\varphi_i = \sum_r C_{ir}\chi_r \qquad (11)$$

where χ_r is the rth valence-shell atomic orbital and C_{ir} its coefficient. Hereafter the suffixes r and s will be used to denote the valence shell atomic orbitals.

(v) The Coulomb repulsion integral between valence electrons and inner-shell electrons is rewritten by introducing the penetration terms

$$
\begin{aligned}
2\sum_i(ii|kk) = \sum_r\sum_s P_{rs}(rs|1/R_k) + \\
\sum_r\sum_s P_{rs}\{(rs|kk) - (rs|1/R_k)\} \qquad (12)
\end{aligned}
$$

where

$$P_{rs} = 2\sum_i^{\mathrm{occ}} C_{ir}C_{is} \qquad (13)$$

$$(rs|1/R_k) = \int \chi_r^*(1)\chi_s(1)1/R_{1k}\mathrm{d}\tau_1 \qquad (14)$$

and $(rs|kk)$ is the Coulomb repulsion integral between the valence-shell atomic orbitals and the inner-shell atomic orbital.

(vi) All the differential overlaps are neglected.

In order to calculate the energy of the valence electrons only, the following modification of the equation was carried out by using eq 12

$$
\begin{aligned}
2\sum_{i=1}^{n}(i|h|i) + 2\sum_i\sum_k\{2(ii|kk) - (ik|ik)\} = \\
& \sum_r\sum_s P_{rs}\Big(\chi_r^*(1)| - {}^1\!/_2\Delta_1 - \sum_k Z_k/R_{1k} - \\
& \sum_h 1/R_{1h}|\chi_s(1)\Big) + 2\sum_r\sum_s\sum_k P_{rs}(\chi_r^*(1)|1/R_{1k}|\chi_s(1)) + \\
& 2\sum_r\sum_s\sum_k P_{rs}\{(rs|kk) - \\
& {}^1\!/_2(rk|sk) - (rs|1/R_k)\} = \sum_r\sum_s P_{rs}(\chi_r^*(1)| - \\
& {}^1\!/_2\Delta_1 - \sum_k(Z_k - 2)/R_{1k} - \sum_h 1/R_{1h}|\chi_s(1)) + \\
& 2\sum_k\sum_{r_k} P_{r_kr_k}\{(r_kr_k|kk) - (r_kr_k|1/R_k)\} \qquad (15)
\end{aligned}
$$

where the summation of h covers over all the hydrogen atoms in the molecule and r_k denotes the valence-state atomic orbital which belongs to the same atom as the inner-shell atomic orbital k. The second term in the right side of eq 15 which represents the penetration effects was obtained by using eq 12 and the approximation of complete neglect of differential overlap. Further, this term contains only the one-center penetration term. The first term includes the core integral for the valence electrons in the electric field of the nuclei and the inner-shell electrons. Therefore, this term can be considered to be the same one that appeared in approximate molecular orbital methods for the valence electrons such as CNDO,[17-19] INDO,[23] and MINDO[24,25] method. The similar modification as eq 15 was carried out for the ionized molecule.

The binding energy for the inner-shell electrons can be obtained by making use of the approximation abovementioned as follows.

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[23] J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967).

[24] N. C. Baird and M. J. S. Dewar, *ibid.*, **50**, 1262 (1962).

[25] M. J. S. Dewar and E. Haselbach, *J. Amer. Chem. Soc.*, **92**, 590 (1970).

$$\begin{aligned}
I_{\mathrm{p}} = \Big[& \sum_{r}\sum_{s} P_{rs}{}^{+}\Big(\chi_r{}^{+*}(1)\Big| - {}^{1}\!/_{2}\Delta_1 - \\
& \sum_{\substack{k\\(\neq t)}}(Z_k - 2)/R_{1k} - (Z_t - 1)/R_{1t} - \\
& \sum_{h} 1/R_{1h}\, \chi_s{}^{+}(1)\Big) + \sum_{i}\sum_{j}\{2(i^{+}i^{+}|j^{+}j^{+}) - \\
& (i^{+}j^{+}|i^{+}j^{+})\}\Big] - \Big[\sum_{r}\sum_{s} P_{rs}\Big(\chi_r{}^{*}(1)\Big| - \\
& {}^{1}\!/_{2}\Delta_1 - \sum_{k}(Z_k - 2)/R_{1k} - \sum_{h} 1/R_{1h}\Big|\chi_s(1)\Big) + \\
& \sum_{i}\sum_{j}\{2(ii|jj) - (ij|ij)\}\Big] + \\
\Big[& 2\sum_{\substack{k\\(\neq t)}}\sum_{r_k} P_{r_kr_k}{}^{+}\{(r_k{}^{+}r_k{}^{+}|kk) - (r_k{}^{+}r_k{}^{+}|1/R_k)\} + \\
& \sum_{r_t} P_{r_tr_t}{}^{+}\{(r_t{}^{+}r_t{}^{+}|t^{+}t^{+}) - (r_t{}^{+}r_1{}^{+}|1/R_t)\} - \\
& 2\sum_{k}\sum_{r_k} P_{r_kr_k}\{(r_kr_k|kk) - (r_kr_k|1/R_k)\}\Big] + \\
& [(\chi_t{}^{+*}(1)| - {}^{1}\!/_{2}\Delta_1 - Z_t/R_{1t}|\chi_1{}^{+}(1)) - \\
& 2(\chi_t{}^{*}(1)| - {}^{1}\!/_{2}\Delta_1 - Z_t/R_{1t}|\chi_t(1)) - \\
& (tt|tt)] + \Big[\sum_{\substack{k\\(\neq t)}}(Z_k - 2)/R_{kt} + \sum_{h} 1/R_{ht}\Big] \qquad (16)
\end{aligned}$$

In eq 16, the first term is the total electronic energy of the closed-shell valence electrons for the ionized molecule and the second term is that for the neutral molecule. The third term is the penetration term, and the fourth term depends only on the species of atoms since there are no terms containing the molecular orbitals of the valence electrons. In other words, this term is constant in magnitude from molecule to molecule and has no contribution to the chemical shifts for the inner-shell binding energy. The last term can be rewritten as follows.

$$\begin{aligned}
\sum_{\substack{k\\(\neq t)}}(Z_{kt} - 2)/R_k + \sum_{h} 1/R_{ht} = \\
& \sum_{\substack{k\\(\neq t)}}\sum_{\substack{l\\(<k)\\(\neq t)}}(Z_k - 2)(Z_l - 2)/R_{kl} + \\
& \sum_{\substack{k\\(\neq t)}}(Z_k - 2)(Z_t - 1)/R_{kt} - \\
& \sum_{k}\sum_{\substack{l\\(<k)}}(Z_k - 2)(Z_l - 1)/R_{kl} + \\
& \sum_{\substack{k\\(\neq t)}}\sum_{h}(Z_k - 2)/R_{kh} + \sum_{h}(Z_t - 1)/R_{th} - \\
& \sum_{k}\sum_{h}(Z_k - 2)/R_{kh} \qquad (17)
\end{aligned}$$

From this equation, it is apparent that the last term of eq 16 is equal to the difference in the core repulsion energy between the ionized and the neutral molecules in the approximate molecular orbital method for valence electrons. Combining eq 16 with eq 17, we obtain the relatively simple formula for the binding energy of the inner-shell electron

$$\begin{aligned}
I_{\mathrm{p}} = {} & \text{constant} + E(\text{ionized molecule}) - \\
& E(\text{neutral molecue}) + 2\sum_{k}\sum_{r_k}(P_{r_kr_k}{}^{+} - \\
& P_{r_kr_k})\{(r_kr_k|kk) - (r_kr_k|1/R_k)\} - \\
& 2\sum_{r_t} P_{r_tr_t}{}^{+}\{(r_tr_t|tt) - (r_tr_1|1/R_t)\} + \\
& \sum_{r_t} P_{r_tr_t}{}^{+}\{(r_t{}^{+}r_t{}^{+}|tt) - (r_t{}^{+}r_t{}^{+}|1/R_t)\} \qquad (18)
\end{aligned}$$

where E(ionized molecule) and E(neutral molecule) are the total energies of the valence electrons in the closed shells for the ionized and the neutral molecules, respectively, which include both the total valence electronic and the total core repulsion energies. The first term, constant, corresponds to the fourth term of eq 16, and hence this term depends only on the species of the atom in question and has no contribution to the chemical shift. The remaining terms in eq 18 are the penetration terms, which were simplified on the assumption that the valence-state atomic orbitals in an ionized molecule are the same as those in the neutral molecule except for the valence-state atomic orbital whose inner-shell electron is ionized.

The obtained formula, eq 18, was applied to the carbon and the nitrogen atoms of DNA bases, that is, adenine, thymine, and cytosine, in order to compare the calculated chemical shifts with the observed ones.[20] E(neutral molecule) and E(ionized molecule) were calculated by using the CNDO/2 method. For the neutral molecules, the parameters involved in the CNDO/2 method are those usually used. For ionized molecules, the situation may be different, since the ionization of the inner-shell electrons will lead to the change of the valence state of the atom in question. Since this change in the valence state is difficult to evaluate quantitatively, two extreme cases were employed in the present calculation. One is that the changes in valence states are taken into account only through the change of the core potential; that is, the parameters involved in the CNDO/2 method are the same as those used for neutral molecules except for the core charge of the ionized atom, which increases by one owing to the ionization of an inner-shell electron.[26] Another approach is that the changes in valence states are considered to correspond to the replacement of the atom by the next right atom in the periodical table. Namely, when the ionization of an inner-shell electron occurs, the valence electrons will feel the core potential which is larger by one than the core potential of the neutral atom; that is, the valence electrons in the ionized carbon atom will feel the same core potential as that of the nitrogen atom. Therefore, the total energies by the CNDO/2 method were calculated with the parameters of the nitrogen atom for the ionized carbon atom, that of the oxygen for the ionized nitrogen, and so on. The former approximation should be suitable for molecules with the relatively small charge redistribution by the ionization; on the other hand, the latter is applicable to those with the relatively large redistribution. The valence-state atomic orbitals, other than the valence-state atomic orbital whose inner-shell electron is ionized, are assumed to remain unchanged upon the ionization of the inner-shell electron. The penetration terms in eq 18 were calculated by using single Slater-type atomic orbitals with its exponent calculated by Slater rule. Although the Slater-type 1s atomic orbital is not orthogonal to the 2s orbital, the approximate estimation of penetration terms in magnitude can

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(26) Strictly speaking, the ionization of an inner-shell electron leads to the change in magnitude of the diagonal element of Fock operator in the CNDO/2 method by subtracting (1s1s|2s2s) instead of (2s2s|2s2s). For simplicity, however, the total energies of ionized molecules are calculated with the increase of the core charge by one, which corresponds to subtracting (2s2s|2s2s) from Fock's diagonal element of neutral molecules.

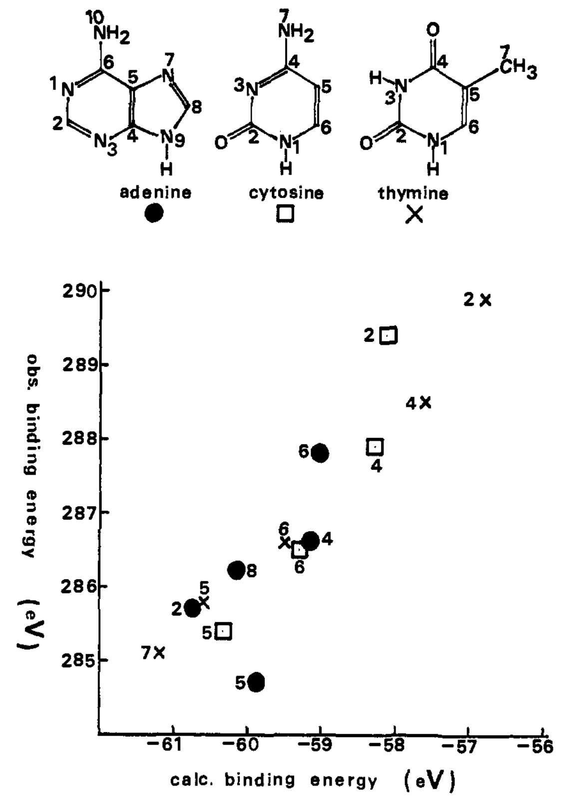

Figure 1. Comparison of the observed binding energies with the theoretical ones calculated with the change of the core charge only (calcn 1 in Table I) for the carbon atoms.

adequately be carried out with Slater orbitals. The first constant term in eq 18 has no relation with the chemical shift; hence, this term was not calculated in the present paper. Accordingly, the calculated values for the binding energies are listed without this constant term in the following section.

Results and Discussion

In Table I, the calculated binding energies of carbon atoms in adenine, thymine, and cytosine are tabulated in comparison with the observed values and the net charges on the corresponding atom in the neutral molecules. It is clear that the contribution of the penetration terms is very small. In order to see the correlation between the theoretical values and the experimental ones, the former is plotted against the latter in Figures 1–3. That is, in Figure 1 the calculated binding energies are obtained in the approximation that only the core charge increases by one, and in Figure 2 the binding energies are calculated with the replacement of the parameters in the CNDO/2 method of the carbon atoms by those of the nitrogen atoms. The charges on the corresponding atom calculated for the neutral molecule were also plotted against the experimental binding energy in Figure 3. The clear correlation between the calculated and the observed values is found in Figure 1; namely, a linear relation with slope of about 45° can be drawn. The similar feature is found

Table I. Binding Energies of Inner-Shell Electrons of Carbon Atoms

Atom[a]	Obsd	Calcn 1[b]	Calcn 2[c]	Penetration[d]	Net charge[e]
A-5	284.7	−59.89	−120.09	0.09	−0.05
T-7	285.1	−61.19	−115.89	−0.03	+0.01
C-5	285.4	−60.34	−117.57	0.07	−0.17
A-2	285.7	−60.75	−119.70	0.08	+0.21
T-5	285.8	−60.60	−117.12	0.10	−0.12
A-8	286.2	−60.14	−119.43	0.08	+0.18
C-6	286.5	−59.30	−116.12	0.07	+0.19
T-6	286.6	−59.51	−116.80	0.05	+0.15
A-4	286.6	−59.16	−119.59	0.09	+0.21
A-6	287.8	−59.05	−119.11	0.09	+0.26
C-4	287.9	−58.28	−117.74	0.09	+0.33
T-4	288.5	−57.62	−119.43	0.12	+0.36
C-2	289.4	−58.13	−121.27	0.12	+0.44
T-2	289.9	−56.81	−119.09	0.13	+0.43

[a] A, C, and T indicate adenine, cytosine, and thymine, respectively. The numberings of the atoms are shown in Figure 1. [b] Calculations with the change of the core charge only. [c] Calculations with the modification of the parameters of the CNDO/2 method. [d] The penetration terms. [e] The net charges in the neutral molecules.

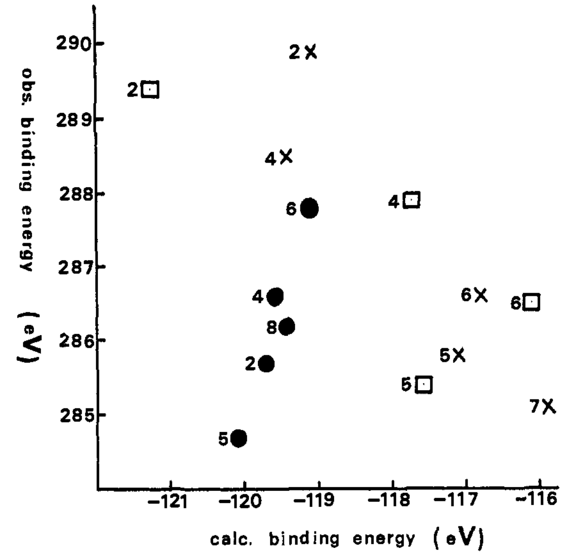

Figure 2. Comparison of the observed binding energies with the theoretical ones calculated with the modification of the parameters in the CNDO/2 method (calcn 2 in Table I) for the carbon atoms. The numberings of the atoms are the same as in Figure 1.

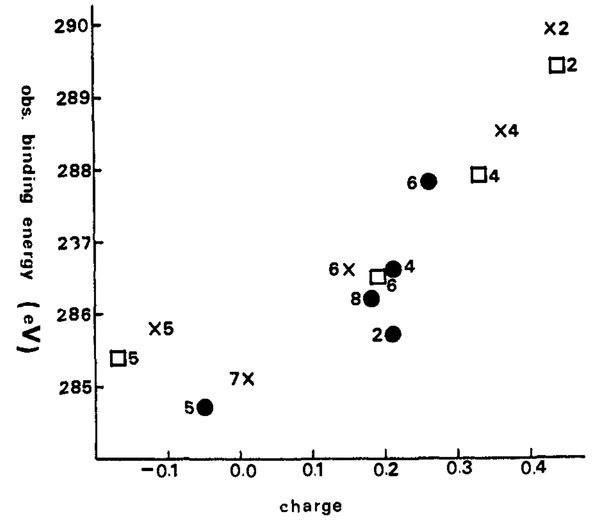

Figure 3. Comparison of the observed binding energies with the net charges in the neutral molecules for the carbon atoms. The numberings of the atoms are the same as in Figure 1.

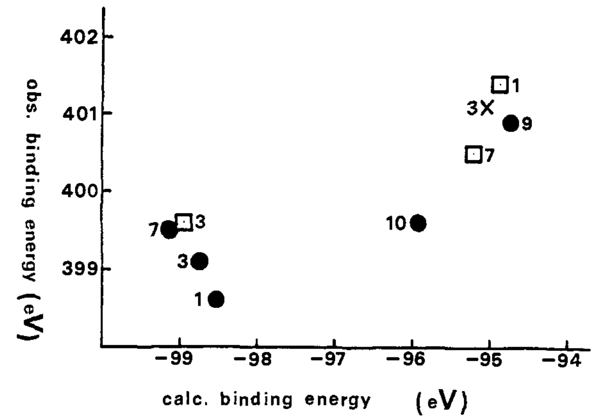

Figure 4. Comparison of the observed binding energies with the theoretical ones calculated with the change of the core charge only (calcn 1 in Table II) for the nitrogen atoms. The numberings of the atoms are the same as in Figure 1.

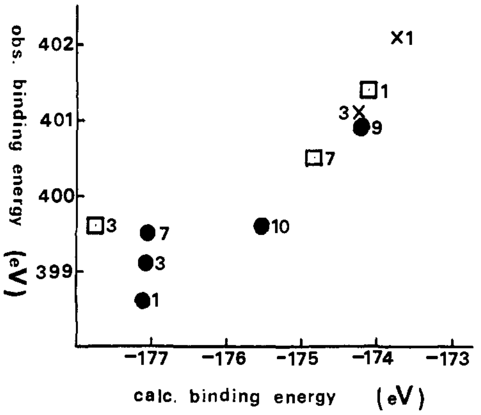

Figure 5. Comparison of the observed binding energies with the theoretical ones calculated with the modification of the parameters in the CNDO/2 method (calcn 2 in Table II) for the nitrogen atoms. The numberings of the atoms are the same as in Figure 1.

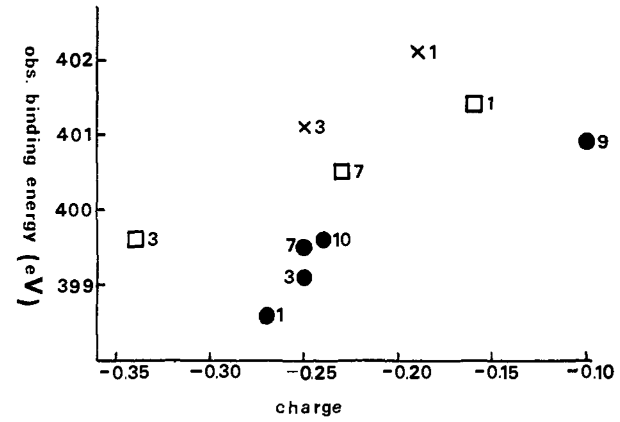

Figure 6. Comparison of the observed binding energies with the net charges in the neutral molecules for the nitrogen atoms. The numberings of the atoms are the same as in Figure 1.

Table II. Binding Energies of Inner-Shell Electrons of Nitrogen Atoms

Atom[a]	Obsd	Calcn 1[b]	Calcn 2[c]	Penetration[d]	Net charge[e]
A-1	398.6	−98.55	−177.13	0.27	−0.27
A-3	399.1	−98.74	−177.09	0.27	−0.25
A-7	399.5	−99.16	−177.06	0.27	−0.25
A-10	399.6	−95.94	−175.55	0.21	−0.24
C-3	399.6	−98.94	−177.74	0.29	−0.34
C-7	400.5	−95.22	−174.84	0.22	−0.23
A-9	400.9	−94.76	−174.23	0.25	−0.10
T-3	401.1	−95.06	−174.25	0.25	−0.25
C-1	401.4	−94.91	−174.13	0.26	−0.16
T-1	402.1	. . .[f]	−173.75	0.26	−0.19

[a] A, C, and T indicate adenine, cytosine, and thymine, respectively. The numberings of the atoms are shown in Figure 1. [b] Calculations with the change of the core charge only. [c] Calculations with the modification of the parameters of the CNDO/2 method. [d] The penetration terms. [e] The net charges in the neutral molecules. [f] The SCF calculation is divergent.

in the relation between the observed binding energy and the charge on the atom in question in Figure 3, although the agreement is slightly dissatisfactory. It is the most striking aspect of the result that the calculated binding energies with the modification of parameters seem to have no relation with the observed binding energies as shown in Figure 2. Consequently the ionization of the carbon inner-shell electron in the DNA bases can be considered to be the relatively small perturbation for the electron distribution and this may be the reason why the calculated values are correlated well with the experimental results in Figures 1 and 3 but *not in* Figure 2.

Next, the binding energies of the nitrogen inner-shell electrons were calculated for adenine, thymine, and cytosine in a similar manner as those for the carbon atoms. The results are shown in Table II and Figures 4–6. As is also the case for the carbon atoms, the penetration term written in the fifth column of Table II is found to be nearly constant and has little contribution to the chemical shift of the nitrogen atoms. Among Figures 4–6, the plot in Figure 5 indicates that the theoretical values reproduce the experimental ones fairly well. On the other hand, the good correlation is not found when calcn 1 was adopted as in Figure 4. Accordingly, the ionization of the inner electron of the nitrogen atom in the DNA bases is considered to give a relatively large effect of the electron redistribution. This result is consistent with the result in Figure 6; that is, the net charges for the neutral molecules have no definite correlation with the observed values. It is of special interest that the chemical shift of the carbon atoms in the DNA bases can be reproduced well with the method of the core charge change and the net charge on the atom, while the chemical shift of the nitrogen atoms should be calculated with the modification of the parameters in the CNDO/2 method. In connection with this, Ishida, *et al.*,[22] had also calculated the chemical shifts of the carbon and the nitrogen atoms obtaining a good correlation with observed values for the carbon atoms but a less satisfactory one for the nitrogen atoms. This result corresponds well with that in the present article, since their method does not include the effect of the electron redistribution and, hence, the results by the approximation of the core charge change in the present paper are expected to correspond approximately to their results.

The reason why the chemical shifts for the carbon and the nitrogen atoms should be calculated by the different approximations may probably be interpreted from the electron distributions before and after the ionization of the inner-shell electrons. In Figure 7,

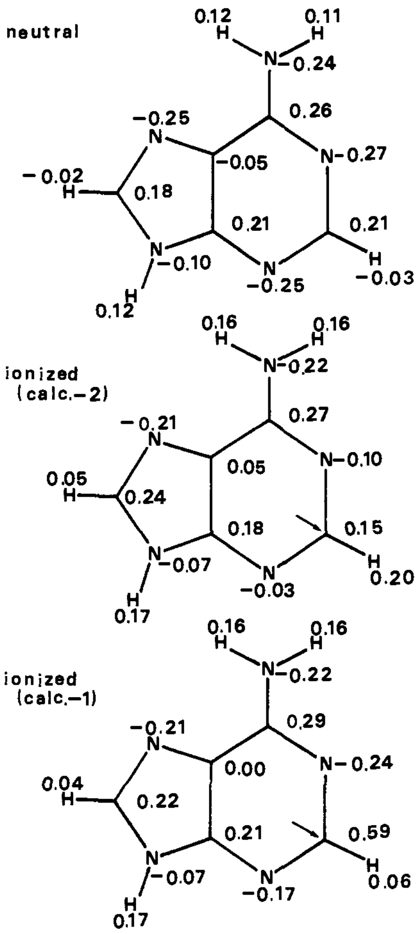

Figure 7. The charge distributions of adenine in the neutral state and in the ionized state by the ionization of the C_2 inner-shell electrons.

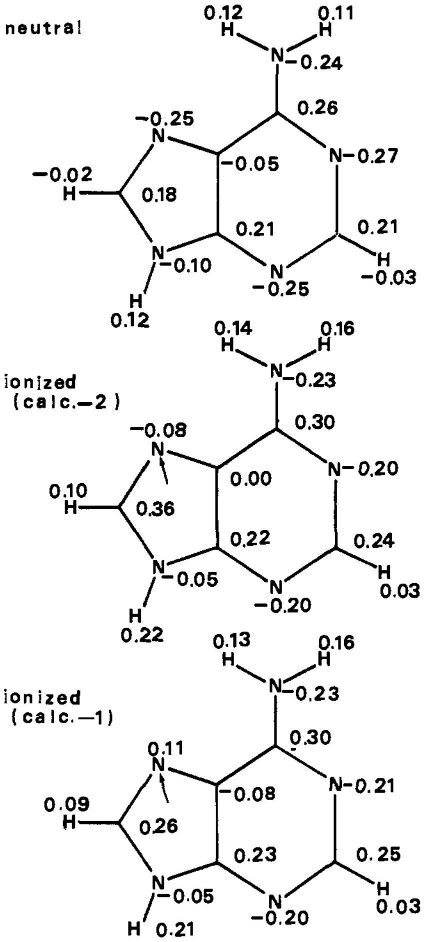

Figure 8. The charge distributions of adenine in the neutral state and in the ionized state by the ionization of the N_7 inner-shell electrons.

the charge distributions of ionized adenine are indicated for the ionization of the inner-shell electron of the C_2 atom in comparison with that of the neutral molecule. The charge distribution after the ionization of the N_7 atom is also indicated in Figure 8. From Figure 7, the charge on the ionized carbon atom (+0.59) calculated by the approximation of the core charge change (calcn 1 in Table I) indicates that the valence-shell electron density of the ionized carbon atom (−4.41) is closer to that of the neutral carbon atom rather than to that of the neutral nitrogen atom. On the other hand, the charge on the N_7 atom (+0.11) in Figure 8 calculated in the same approximation (calcn 1 in Table II) has the valence-shell electron density (−5.89) which is close to that of oxygen atom. The difference in the charge distribution between the ionized carbon and the nitrogen atoms should generally be due to the positive charges of carbon atoms and the negative charges on nitrogen atoms of the DNA bases in the neutral states. From the viewpoint of the charge distributions, the parameters in the CNDO/2 method for the carbon atom are appropriate for the calculation of the chemical shift of the carbon atoms in the DNA bases, while those for the oxygen atom have to be applied for the chemical shift of the nitrogen atoms in complete agreement with the results obtained in this article.

In conclusion, the method and the approximations used in the present paper can give the excellent agreement with the experimental data for the chemical shifts of the carbon and the nitrogen atoms in the DNA bases by using different parameterizations for the carbon and the nitrogen atoms, respectively. The use of the different parameterization can be rationalized from the charge distributions of the molecules before and after the ionization of an inner-shell electron. In connection with this conclusion, the applicability of the present method to other molecules than the DNA bases is under investigation as well as the extension of this method to the calculation of the binding energy of oxygen atoms in various molecules. One technical problem to be solved in the present method is that SCF calculations for ionized molecules sometimes diverge, especially for small molecules. These will be published in the future. There can be a more elaborate treatment which gives more complete agreement with the experiment; that is, the variable electronegativity-like[27] treatment in the CNDO/2 method may be a more general and excellent method.

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