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An MO Interpretation of the Chemical Shifts of the Binding Energies of Inner-shell Electrons. II. A Study of Intramolecular Shifts

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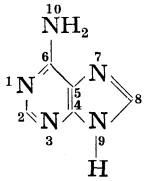
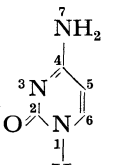
The relationship between chemical shifts in the binding energies of inner-shell electrons and molecular-charge distributions has been pointed out.[1] For adenine and cytosine molecules, however, Barber and Clark[2] concluded that a "simple relationship between 'shifts' in binding energies and 'charge distributions' can be misleading." In a previous paper,[3] we have derived the following correlation formula between the chemical shifts and molecular-charge distributions within a MO framework:

$$\delta\Delta\varepsilon_s(X, Y) = [Q_A(X) - Q_A(Y)]\gamma_{AA} + \sum_{B(\neq A)}^{\text{in } X} Q_B(X)\gamma_{AB}(X) - \sum_{B(\neq A)}^{\text{in } Y} Q_B(Y)\gamma_{AB}(Y)$$

where $\delta\Delta\varepsilon_s(X,Y)$ denotes the chemical shifts of an inner-shell electron, s, on an atom, A, in a chemical environment, X, from that in another environment, Y. $Q_A(X)$, $Q_B(Y)$, and so on denote the net charges on the A, B, *etc.* atoms in the X, Y, *etc.* environments respectively. γ_{AA} denotes a one-center average Coulomb interaction between inner and valence electrons on an A atom. $\gamma_{AB}(X)$ denotes a two-center average Coulomb interaction between inner electrons on an A atom and valence electrons on a B atom in an X environment.

For inter-molecular shifts of simple molecules, the results by the above formula almost entirely accorded with the experimentally obtained values. In the present note, we will report an application of the above formula to the intra-molecular shifts of adenine and cytosine molecules. The results are shown in Table 1 for carbon 1s and nitrogen 1s. Figures 1 and 2 show the plots of the observed binding energies against the calculated $\Delta\varepsilon_s$[4] values for carbon 1s and for nitrogen 1s respectively. The figures illustrate that the correlations are fairly satisfactory. Especially, the correlation is quantitatively good for the carbon 1s of adenine in Fig. 1, in view of the fact that the solid line is drawn at 45 degree with respect to the horizontal axis. For the nitrogen 1s, the correlations are rather good, but not quantitative, as shown in Fig. 2. In view of the non-empirical calculations done on limited bases by Mely and Pullman[5] and by Clementi,[6] deviation of the observed binding energy from the calculated orbital energy can be not said to be constant (except for the carbon 1s of adenine). Therefore, the different slopes in Fig. 2 most probably arise from the fact that the above deviation is not constant.

TABLE 1. CALCULATED $\Delta\varepsilon_s$ AND OBSERVED BINDING ENERGIES

Molecule	1s Binding		
	Atom	Energy[a] (±0.3 eV)	$\Delta\varepsilon_s$ (eV)
	C-5	284.7	−0.44
	C-2	285.7	1.63
	C-8	286.2	1.88
	C-4	286.6	2.40
	C-6	287.8	3.04
	N-1	398.6	−5.98
	N-3	399.1	−4.68
	N-7	399.5	−2.67
	N-10	399.6	−4.73
	N-9	400.9	1.24
	C-5	285.4	−0.28
	C-6	286.5	3.29
	C-4	287.9	4.75
	C-2	289.4	4.22
	N-3	399.6	−5.87
	N-7	400.5	−1.90
	N-1	401.4	−1.33

a) M. Barber and D. T. Clark, *Chem. Commun.*, **1970**, 22, 24.

1) *E.g.* K. Siegbahn *et al.*, ESCA "Atomic Molecular and Solid State Structure Studied by Means of Electron Spectroscopy," Almquist and Wiksells, Uppsala, (1967); D. M. Hercules, *Anal. Chem.*, **42**, 20A (1970).

2) M. Barber and D. T. Clark, *Chem. Commun.*, **1970**, 22.

3) H. Kato, K. A. Ishida, H. Nakatsuji, and T. Yonezawa, This Bulletin, **44**, 2587 (1971).

4) We calculated the $\Delta\varepsilon_s$ with $\Delta\varepsilon_s(X) = Q_A(X)\gamma_{AA} + \sum_{B(\neq A)}^{\text{in } X} Q_B(X) \cdot \gamma_{AB}(X)$, using approximate net charges which has been obtained by the CNDO/2 method.

5) B. Mely and A. Pullman, *Theor. Chim. Acta*, **13**, 278 (1969).

6) E. Clementi, *Int. J. Quant. Chem.*, **IIIs**, 179 (1969).

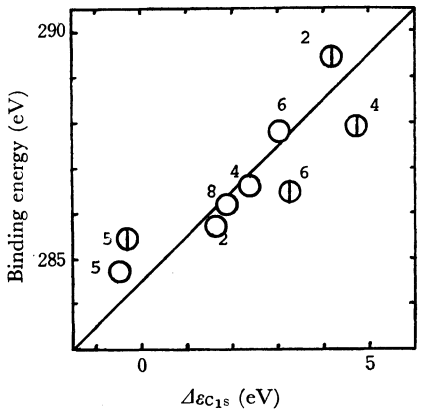


Fig. 1. Observed binding energy *vs.* calculated $\Delta\varepsilon_s$ plots for carbon 1*s* in adenine and cytosine.

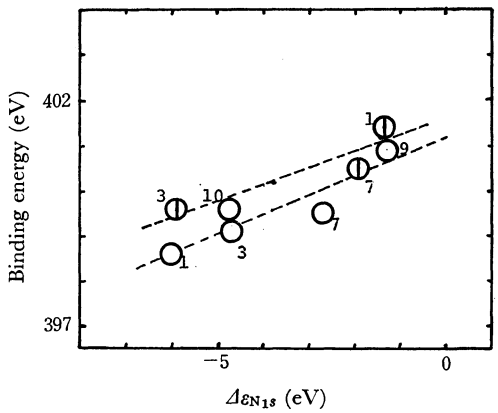


Fig. 2. Observed binding energy *vs.* calculated $\Delta\varepsilon_s$ plots for nitrogen 1*s* in adenine and cytosine.

The above formula means that the chemical shifts of the binding energies should be correlated with charge distributions, though not with simple local charges. Therefore, the previously-refered to suggestion by Barber and Clark is not valid in the present case.

From the above brief discussions we conclude that our formula is useful for the assignment of intra-molecular shifts so long as approximate net charges obtained by a semi-empirical method are used.