Intermolecular Charge—Transfer Spectra. III. Organic Molecular Complexes

By Hideo MURAKAMI

(Received January 1, 1954)

In recent years, quantitative experimental studies have been undertaken concerning the absorption spectra and equilibrium constants of organic molecular complexes. We can expect that the theoretical analysis of these results will provide us with more precise information than before for their electronic structure especially for the mutual interactions between two components. In the first and second sections, we will discuss the magnitude of resonance interaction in relation with the intensities of intermolecular charge-transfer spectra. Next, the contribution of non-resonance interactions, such as van der Waals type interaction and various electrostatic interactions will be considered in comparison with the former.

The Relation between Absorption Intensity and Resonance Interaction

As is easily seen, the straightforward and quantitative calculation of resonance energy between two components is very difficult on account of the extreme complexity of the electronic system and uncertainty of the radial part of the constituent atomic wave function. It is not difficult, however, to obtain a formula which gives us a resonance interaction energy in terms of absorption intensity. Since the latter quantity is known experimentally, this formula enables us to estimate the magnitude of the former.

In the first paper of this series[1] (in the following, we refer to I) we summarized the essence of Mulliken's theory of intermolecular charge-transfer spectra in the approximation which neglects the overlap integral S between two components. In the following ,we use the simplified formulae in I, since the neglect of S does not affect the final results. According to Mulliken's theory[2], the wave function of the ground state of any molecular complex $(A\ B)$ is given by

$$\psi_N = a\,\psi_0 + b\,\psi_1 \tag{1}$$

where ψ_0, ψ_1 is defined respectively

$$\psi_0 = \psi(A\cdot B),\quad \psi_1 = \psi(A^- - B^+)$$

In case of loose complex ($a^2 \gg b^2$), the energy of the ground state becomes as follows,

$$W_N \simeq W_0 - H_{01}{}^2/(W_1 - W_0) \tag{2}$$

where $-H_{01}{}^2/(W_1-W_0)$ corresponds to the resonance interaction energy and W_0 includes the exchange repulsive interaction energy together with various non-resonance interaction energies. (The derivation of Eq. (2) and the definition of W_0, W_1 and H_{01} are given in I. See Eqs. (5), (6), (7), (8) and (9) in I). From I(11), it follows

$$H_{01}{}^2/(W_1 - W_0) \simeq b^2(W_1 - W_0)/a^2 \tag{3}$$

Further, from I (12), we obtained the relation

$$\mu_{EN}/e = Q_{EN} \simeq ab(\vec{r}_B - \vec{r}_A)$$

or

$$b^2 \simeq Q^2{}_{EN}/a^2(\vec{r}_B - \vec{r}_A)^2 \tag{4}$$

Eqs. (3) and (4) provide us with the relation

$$H_{01}{}^2/(W_1 - W_0) \simeq Q^2{}_{EN}(W_1 - W_0)/a^4(\vec{r}_B - \vec{r}_A)^2 \tag{5}$$

On the other hand, oscillator strength f_{EN} of transition ($E \rightarrow N$) is given by

$$f_{EN} = (8\pi^2 mc/3h)\nu Q^2{}_{EN}$$

From this

$$Q^2{}_{EN} = (3h/8\pi^2 mc) f_{EN}/\nu \tag{6}$$

where

$$1/\nu = \lambda = ch/(W_E - W_N)$$

In case of loose complex, we can expect the relation

$$W_E - W_N \simeq W_1 - W_0 \tag{7}$$

The combination of Eqs. (5), (6) and (7) provides us with the formula

$$H_{01}{}^2/(W_1 - W_0) \simeq (3h^2/8\pi^2 m) f_{EN}/a^4(\vec{r}_B - \vec{r}_A)^2 \tag{8}$$

If we assume

$$a \simeq 1$$

Eq. (8) is simplified as follows:

$$\begin{aligned} H_{01}{}^2/(W_1 - W_0) &\simeq (3h^2/8\pi^2 m) f_{EN}/(\vec{r}_B - \vec{r}_A)^2 \\ &= 11.5 \times 10^{-16} f_{EN}/(\vec{r}_B - \vec{r}_A)^2 ev \end{aligned} \tag{9}$$

In this approximation, the resonance energy is proportional to oscillator strength f_{EN} of intermolecular charge-transfer spectra and does not include the energy quentity explicitly.

In order to obtain the absolute value of the intermolecular charge-transfer interaction energy, we should take into account not only the attractive term of Eq. (8) or (9) but also the exchange repulsive term which is included in W_0 in Eq. (2). As can easily be inferred, the factors which enlarge the attractive term through the increase of H_{01} also produce the increase of exchange repulsive term by almost the same amount. Then we can expect that these two terms which have opposite signs and the nearly equal absolute value will cancel each other almost completly. This situation may probably enable us to explain the relatively large absorption intensity and the relatively small heat of formation of iodine-benzene complex.

---

[1] H. Murakami, This Bulletin, **26**, 441 (1953).

[2] R. S. Mulliken, *J. Am. Chem. Soc.*, **74**, 811 (1952).

Analysis of the Experimental Results

The absorption spectra and equilibrium constants between two components have been observed for various types of organic molecular complexes by many workers.[3-7] Their results are shown in Table I together with the representative data on halogen-aromatic complexes.[8-11] They emphasized the proportional relation between equilibrium constant K and the donor character of B-component (or the acceptor character of A-component). Since equilibrium constant K is the measure of stability of complex (strictly speaking in case of the same solvent and equal temperature), the increase of K implies the increase of attractive interaction energy. On the other hand, the increase of donor character of B-component or acceptor character of A-component seems to produce the increase of resonance interaction energy through the decrease of (W_1-W_0). (See Eq. (2)). Considering these facts, they concluded that the intermolecular charge-transfer interaction was contributing to molecular complex formation as the most essential factor.

If this is the case, Eq. (8) or (9) predicts the increase of f_{EN} with increase of K. As is well known, f_{EN} can be related with molar extinction coefficient by the formula.

$$f_{EN}=(mc^2/N\pi e^2)\cdot 10^3\int\varepsilon_\nu d\nu/\log_{10}e$$
$$\simeq 4.32\times10^{-9}\,\varepsilon_c\Delta\nu \qquad (10)$$

where $\Delta\nu$ is the half-breadth of absorption curve. Then, one has to expect the increase of ϵ_c with increase of K so long as the magnitude of $\Delta\nu$ is approximately the same for respective class of complexes. According to the data in Table I, the experimental results predict the reverse. That is, the increase of K is accompanied with the decrease of ϵ_c without exception.* In order to avoid this contradiction, one has to postulate that the contribution of intermolecular charge-transfer interaction to the total binding energy is rather smalll compared with that of the other types of

TABLE I

EXPERIMENTAL DATA FOR VARIOUS TYPES OF MOLECULAR COMPLEXES

A-Component	B-Component	Solvent	λ_{max} (Å)	ϵ_c	K	(Temperature)	Reference
s-Trinitrobenzene	Benzene	n-Heptane	2800	~4000	4.09	(21.5°)	(5)
	Aniline	Chloroform	~4000	~1550	5.1	(22°)	(4)
Oxalyl Chloride	Benzene	Heptane	2800	3333	0.27		(3)
p-Quinone	Benzene	Chloroform	2800~2900	(2800)[a]	0.42	(25°)	(7)
	Phenol	Cyclohexane	3150	1200	(0.93)[b]	(25°)	(6)
	Hydroquinone	0.05 M HCl aq. solution	4400	890	(0.97)[b]	(25°)	"
	Dimethylhydroquinone	Cychohexane	4130	370	0.60	(25°)	"
Maleic anhydride	Benzene	Chloroform	2760	3140	0.68	(25°)	(7)
	Anisol	"	3000	2020	0.84	(")	"
	Dimethylaniline	"	4140	1590	1.5	(")	"
Iodine	Benzene	Carbon Tetra-Chloride	2970	15400	1.72	(22°)	(8)
				14000	1.95	(25°)	(9)
Bromine	Benzene	Carbon Tetra-Chloride	2920	13400	1.04	(25°)	(10)
Chlorine	Benzene			9090	0.33	(25°)	(11)

[a] Extrapolated value [b] Interpolated value

---

[3] B. D. Saksena and R. E. Kagarise, *J. Chem. Phys.*, **19**, 994 (1951).

[4] J. Landauer and H. McConnell, *J. Am. Chem. Soc.*, **74**, 1221 (1952).

[5] D. M. G. Lawrey and H. McConnell, *J. Am. Chem. Soc.*, **74**, 6175 (1952).

[6] H. Tsubomura, This Bulletin, **26**, 304 (1953).

[7] L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **75**, 3776 (1953).

[8] H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2703 (1949).

[9] T. M. Cromwell and R. L. Scott, *J. Am. Chem. Soc.*, **72**, 3825 (1950).

[10] R. M. Keefer and L. J. Andrews, *J. Am. Chem. Soc.*, **72**, 4677 (1950).

[11] L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **73**, 462 (1951).

* In order to calculate the absorption intensity f_{EN} or ϵ_c, one should take into account not only the relative orientation of two components but also the following factors: 1) electron density distribution in the molecular orbitals which are essential for the intermolecular charge-transfer spectra 2) the degree of extension of each atomic orbital (for example, $2p$-function of oxygen atom is much reduced in the degree of extension than that of carbon atom). It is easy to show that these two factors make the value of $|H_{01}|$ and consequently that of ϵ_c smaller for the substituted benzene complex than that for benzene complex even if the most compact relative orientation (such as Model (α) or (β)—see later discussion) is assumed.

interactions.

Moreover, the molar extinction coefficients ϵ_c of organic molecular complexes are much smaller than those of halogen-aromatic complexes, that is about 1/10 for many cases. This fact seems to indicate to us the smallness of the intermolecular charge-transfer interaction in organic molecular complexes. Even in case of halogen-aromatic complexes, we postulated in I that the contribution of intermolecular charge-transfer interaction is negligibly small compared with that of van der Waals type interaction. Thus, in case of solution at least, we can conclude that the contribution of resonance type interaction in organic molecular complexes may be very small and the increase of *K* with increase of donor character of *B*-component may be due to the contribution of some other sorts of interactions.

In case of crystal, however, we cannot give any conclusion as to whether the contribution of intermolecular charge-transfer interaction is very small or predominant. Contrasting to the isolated 1 : 1 complex in solution, one molecule comes in contact with several partner molecules in case of crystal. Moreover, as was emphasized by Mulliken, intermolecular charge-transfer force has rather sharp orientational effect.²⁾ Consequently, there may be a case in which the relative orientation of components is governed by this force in crystal.

Non-Resonance Interactions

a) Dipole-Induced Dipole Interaction. It is evident that the van der Waals type interaction is contribution to the binding energy between two components in any molecular complex. According to our opinion, this interaction is most predominant in general. We must notice, however, that van der Waals type interaction is not characteristic for molecular complex but common for every case.

As one of the characteristic interactions, Briegleb emphasized the importance of dipole-induced dipole interaction for the molecular complexes in which *A*-component is polynitrobenzene and *B*-component is polynuclear aromatic hydrocarbon.¹²⁾ The relatively large dipole moment of NO_2 group and the large polarizability of polynuclear aromatic hydrocarbon seems to be suitable for this type of interaction. Briegleb calculated the magnitude of this interaction energy for some examples assuming the intermolecular distance as 3 Å. A part of his results is shown in Table II together with the observed heat of formation.

It is interesting to observe that the calculated and observed values of *p*-dinitrobenzene complex are smaller than any other case for the same *B*-component. This situation can be understood if we consider the relatively great distance between two NO_2 groups and the cancellation of two dipole fields due to the antiparallel orientation of two groups. Assuming the validity of the relation

TABLE II

CALCULATED DIPOLE-INDUCED DIPOLE INTERACTION ENERGY *W* AND OBSERVED HEAT OF FORMATION ΔH IN $C_2H_2Cl_4$. (IN KCAL/MOL). BOTH DUE TO BRIEGLEB ET AL.¹²⁾

A-Component	*B*-Component Anthracene	
	W	ΔH in $C_2H_2Cl_4$
o-Dinitrobenzene	3.0	2.9
m-Dinitrobenzene	1.6	1.5
p-Dinitrobenzene	1.45	1.2
s-Trinitrobenzene	4.6	3.6

W of *s*-Trinitrobenzene·Benzene Complex is 1.8 kcal mol

$$\frac{W\ (s\text{-trinitrobenzene}\cdot\text{benzene complex})}{W\ (s\text{-trinitrobenzene}\cdot\text{anthracene complex})} \fallingdotseq \frac{W\ (p\text{-dinitrobenzene}\cdot\text{benzene complex})}{W\ (p\text{-dinitrobenzene}\cdot\text{anthracene complex})}$$

the magnitude of dipole-induced dipole interaction energy *W* for the case of *p*-dinitrobenzene · benzene complex is estimated as 0.57 Kcal/mol. If we replace *p*-dinitrobenzene with *p*-benzoquinone, this value may reduce to about 2/3, that is about 0.3∼0.4 Kcal/mol on account of the smaller value of dipole moment of CO group than that of NO_2 group.

On the other hand, the magnitude of van der Waals type interaction between two benzene molecules in the most compact orientation is estimated as about 3 Kcal/mol.¹³⁻¹⁵⁾ Then, in case of quinone · benzene or quinone · substituted benzene complex, the magnitude of van der Waals type interac-

---

12) G. Briegleb, *Z. physik. Chem.*, **31**B, 58 (1936). G. Briegleb, "Zwischenmolekulare Kräfte und Molekülstruktur," Stuttgart, (1937).

13) J. H. de Boer, *Trans. Faraday Soc.*, **32**, 10 (1936).

14) V. Myers, *Phys. Rev.*, **78**, 348 (1950).

15) H. A. Stuart, "Die Strucktur des Freien Moleküls", Berlin, (1952). (See p. 78)

tion may probably be ten times as great as that of dipole-induced dipole interaction. Consequently, we can expect that the relative orientation of both components in these complexes is determined by van der Waals type interaction almost completely, at least in case of solution. As is well known, two molecules which attract each other by means of van der Waals' forces will always have a tendency to orient themselves into a position where the largest possible number of atoms are in contact with each other. Thus for the case of quinone *p*-disubstituted benzene complex, we can expect the relative orientation as in Model (β). (See Fig. 2.)

b) Electrostatic Interaction In 1949, Akabori and Murakami pointed out the importance of electrostatic interaction between two components which have the complementary charge distribution.[16] For example, *p*-benzoquinone and *p*-distituted benzene (in which substituents $X^{(B)}$ are CH_3, OH, NH_2, etc.) has charge distribution as shown in Fig. 1 (1) and (2) respectively on account of the resonance effect of π-electron system. If we bring them in the relative position as in Model (β) charges of opposite sign comes nearer than in the case of any other relative orientation. Such a situation as the above suggests the contribution of Coulombic electrostatic interaction together with the van der Waals type interaction. Of course, this type of interaction is characteristic for the molecular complexes and does not exist between the same molecules.

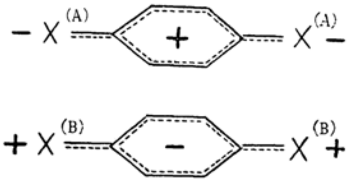

Fig. 1

Now we estimate the magnitude of this electrostatic interaction energy by using a point charge model. As simple and practical cases, we consider Model (α) and Model (β) which are shown in Fig. 2. We assume that each substituent $X^{(A)}$ of *A*-component has charge $-q_a$ (in electrostatic unit) and each substituent $X^{(B)}$ of *B*-component has charge q_b (also in electrostatic unit). Further, in order to simplify the calculation, we assume the uniform charge distribution in the benzene ring.

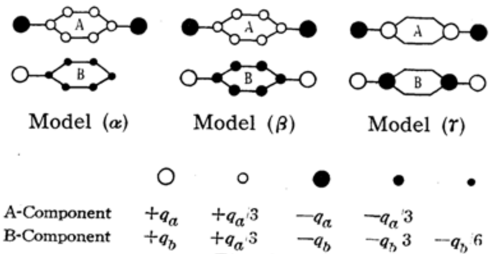

Fig. 2

Then, each carbon atom in the benzene ring of *A*-component has the charge $q_a/3$, and that of *B*-component has the charge $-q_b/6$ in Model (α) and $-q_b/3$ in Model (β). We assume that the intermolecular distance is 3 Å as was taken by Briegleb and the interatomic distances are all 1.39 Å for simplicity. Including all the attractive and repulsive interaction, we obtain the total electrostatic energy $V^{(\alpha)}$ and $V^{(\beta)}$ for Model (α) and (β) respectively as follows:

$$V^{(\alpha)}=V^{(\beta)}/2=-0.100\times10^{8} \qquad (11)$$

If we replace q_a and q_b with x_a and x_b which is defined by

$$q_a=ex_a,\quad q_b=ex_b$$

Eq. (11) becomes as follows:

$$V^{(\alpha)}=V^{(\beta)}/2=-1.45\,x_a x_b\,\mathrm{ev}$$
$$=-33.4\,x_a x_b\,\mathrm{Kcal/mol} \qquad (11a)$$

As another idealized model, we consider the case in which the charges in benzene ring are concentrated on 1-and 4-carbon atoms with equal proportion (Model (γ)). In this case, the straightforward calculation give the relation

$$V^{(\gamma)}\doteqdot 3V^{(\beta)}/4 \qquad \cdots\cdots(12)$$

Then, we can infer that the actual value is situated between $V^{(\beta)}$ and $V^{(\gamma)}$ in the cases of quinone *p*-disubstituted benzene type complexes.

The remaining task is to evaluate the magnitude of x_a and x_b for the respective molecule. Although the various methods can be adopted for this object, Sklar's method seems most attractive. According to Sklar[17] and Herzfeld[18], x_b of monosubstituted benzne is given by

$$x_b=\sum_j \Lambda_j^2 \qquad j=2,3 \qquad (13)$$

$$\Lambda_j=\frac{\rho_j-\omega S_j}{\omega-\omega_j} \qquad (14)$$

where

$$\omega=W+(\zeta\mid \boldsymbol{H}_R\mid\zeta) \qquad (15)$$

$$\omega_j=W_j+(\varphi_j\mid \boldsymbol{H}_{X^{(B)}}\mid\varphi_j) \qquad (16)$$

---

[16] S. Akabori and H. Murakami, *Kagaku-no-Ryoiki* (*The Journal of Japanese Chemistry*), **3**, 10 (1949).

[17] A. L. Sklar *J. Chem. Phys.* **7**, 984 (1939).

[18] K. F. Herzfeld, *Chem. Rev.*, **41**, 233 (1947).

$$\rho_j=\frac{1}{2}[S_j(W+W_j)+(\varphi_j \mid \boldsymbol{H}_R+\boldsymbol{H}_{X^{(B)}} \mid \zeta)] \quad (17)$$

$$S_j=(\varphi_j \mid \zeta)$$

Here ω_j, ω are the energies of the orbitals in benzene ring R and in substituent $X^{(B)}$ as modified by the coulombic contribution of the other part, that is $X^{(B)}$ and R respectively, S_j the overlap between unoccupied orbital φ_j in R and occupied orbital ζ in $X^{(B)}$, and ρ_j the exchange integral. Numerical results for the cases of $X^{(B)}=OH$ and NH_2 have been carried out by Herzfeld,[18] Nagakura and Baba[19], and $x_b=0.075$ and 0.154 respectively. In case of $X^{(B)}=CH_3$,Ri and Eyring obtained the value $x_b=0.027$ from the rate of nitration of substituted benzene.[20] According to Herzfeld, the effect of more than one substitution ought to be additive as long as the values of Λ_j are sufficiently small. Then, we use twice these values for disubstituted benzene. (In case of $X^{(B)}=NH_2$, this assumption may be slightly overestimated). The charge distribution of quinone has been calculated by Nagakura and Kuboyama by the molecular orbital method.[21] Their result indicates $x_a=0.503$.

Introducing these values into Eq. (11a), the electrostatic interaction energies for Models (α), (β) and (γ) are easily obtained, and shown in Table III. The increase of interaction energy with increase of donor character of B-component may enable us to explanin the behavior of equilibrium constant K in Table I. It is evident that these interaction energies are the same order of magnitude as the dipole-induced dipole interaction energies in the case of polynitrobenzene · polynuclear aromatic hydrocarbon complexes.

TABLE III

CALCULATED ELECTROSTATIC INTERACTION ENERGY V IN KCAL/MOL

$X_{(B)}$	Model (α)	Model (β)	Model (γ)
CH_3	0.45	0.9	0.7
OH	1.25	2.5	1.9
NH_2	2.6	5.2	3.9

Appendix

In order to complete the above discussion, we shall consider the correction factors which promote or prevent the electrostatic interaction.

Firstly, we consider the polarization effect as promoting factor. Qualitatively, it is easy to see the increase of charge separation in each component as a result of interaction between complementarily distributed charges. Here, we give a semi-quantitative discussion from the viewpoint of Eqs. (14), (15), (16) and (17). If we express the electrostatic perturbation term from the neighbouring partner molecule by $\boldsymbol{H}'$, ω and α_j in the perturbed state is given by

$$\omega'=W+(\zeta \mid \boldsymbol{H}_R+\boldsymbol{H}' \mid \zeta) \quad (18)$$

$$\omega_j'=W_j+(\varphi_j \mid \boldsymbol{H}_X+\boldsymbol{H}' \mid \varphi_j) \quad (19)$$

$$\omega'-\omega_j'=(\omega-\omega_j)+[(\zeta \mid \boldsymbol{H}' \mid \zeta)-(\varphi_j \mid \boldsymbol{H} \mid \varphi_j)] \quad (20)$$

Then, For example, we assume that $\boldsymbol{H}'$ is the electrostatic perturbation from A-component to an electron in B-component. In this case, $(\zeta \mid \boldsymbol{H}' \mid \zeta)$ represents the decrease of effective ionization potential of substituent $X^{(B)}$ and $(\varphi_j \mid \boldsymbol{H}' \mid \varphi_j)$ represents the increase of effective electron affinity of benzene ring. (More strictly speaking, that of orbital φ_j in the ring). Elementary calculation shows that the numerical value of

$$(\zeta \mid \boldsymbol{H}' \mid \zeta)-(\varphi_j \mid \boldsymbol{H}' \mid \varphi_j)$$

is approximated by Eq. (11a) in which $x_b=-1$ and $x_a=0.503$ (the value for quinone). Then, for Model (α), we obtain the relation

$$\omega'-\omega_j'=(\omega-\omega_j)-0.73\ \text{ev}$$

According to Sklar and Herzfeld,

$$\omega-\omega_j=12.5-7.6=4.9\ \text{ev}, \ (j=2)$$

$$\Lambda_j=0.184$$

for phenol ($X^{(B)}=OH$). By using Eq. (14), these values give us

$$\rho_j-\omega\ S_j=0.902\ \text{ev}$$

In the first approximation, we assume that this value is not changed by the electrostatic perturbation. Then, perturbed value of Λ_2 is given by

$$\Lambda_2'=\frac{\rho_j-\omega\ S_j}{\omega'-\omega_j'}=0.216$$

The relative change of electron density in the ring is given by

$$(\Lambda_2'/\Lambda_2)^2=1.38$$

We should emphasize that this value is rather the lower limit since the increase of the term $(\rho_j-\omega\ S_j)$ through the decrease of ω is neglected. It is not unreasonable to expect that the actual value of $(\Lambda_2'/\Lambda_2)^2$ exceeds 1.5. Analogous effect (though its magnitude may be small) can also be expected for A-camponent. It is evident that these situations contribute to the electrostatic interaction as promoting factor.

Next, we consider the induction effect. For the case of $X^{(B)}=OH$, some workers pointed out that the induction effect in σ-electron system might act as preventing factor.[22,23] This is the case. In OH group, however, the electron affinity of oxygen atom is reduced on account of the relatively large charge transfer from hydrogen into oxygen. Then, one can expect that the amount of σ-electron which is absorbed from neighbouring carbon by oxygen is not so great as is expected

---

[19] S. Nagakura and H. Baba, *J. Chem. Soc. Japan*, **71**, 527 (1950).

[20] T. Ri and H. Eyring, *J. Chem. Phys.*, **8**, 433 (1940).

[21] S. Nagakura and A. Kuboyama, *J. Chem. Soc. Japan* **74**, 499 (1953).

[22] K. Higasi, *Yakugaku Kenkyuu*, **21**, 143 (1949).

[23] K. Suzuki and S. Seki, This Bulletin, **26**, 372 (1953).

from the bond moment 0.81 D of C—O bond. As is well known, this bond moment is obtained from the dipole moment of dimethyl-ether and cannot be used as that of C—O bond in C—OH group. In case of $X^{(B)}=NH_2$, electron affinity of the nitrogen atom is much smaller than that of the oxygen atom. Moreover, there are two hydrogen atoms which reduce the effective electron affinity of the nitrogen atom. Accordingly, the induction effect may probably be negligible for C—N bond in $C—NH_2$ group.

The author wishes to express his sincere gratitude to Prof. S. Akabori for his ceaseless interest and encouragement throughout the course of this series.

Department of Chemistry Faculty of Science, Osaka University, Osaka