Correlation between Two Molecular Orbital Theories on Organic Reactions. I. Ionic Substitutions*

By Hiroaki BABA

(Received October 26, 1956)

Introduction

Among the theories which treat the reactivity of organic molecules on the basis of the method of molecular orbitals, the static and localization theories are extensively used. As was pointed out by Wheland[1], the basic assumptions of the two theories are entirely different and run to two opposite extremes. That is, in the static theory[2-5] the measure of the activity in substitution reactions is the π-electron density, the self-polarizability, or the free valence of the atom to be attacked. All these quantities refer to the normal state of the molecule. On the other hand, the corresponding measure in the localization theory[1,5] is the localization energy. The

---

* Read at the Symposium on π-Electron Problems held by the Chem. Soc. Japan, Oct. 1954 (See Abstract of the Meeting, p. 60). A part of this paper, in Japanese, is to be found in K. Higasi and H. Baba, "Quantum Organic Chemistry", Asakura Publishing Company, Tokyo (1956), p. 314.

1) G. W. Wheland, *J. Am. Chem. Soc.*, **64**, 900 (1942).

2) G. W. Wheland and L. Pauling, *J. Am. Chem. Soc.*, **57**, 2086 (1935).

3) C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.*, **A191**, 39 (1947); **A192**, 16 (1947).

4) C. A. Coulson, *Faraday Soc. Discussion*, No. **2**, 9 (1947).

5) R. D. Brown, *Quart. Rev.*, **6**, 63 (1952).

latter quantity has been presumed by the authors of the theory to be associated with the actual " transition state ".

Notwithstanding the above situation, the same conclusions were reached by the route of each of the two theories. Both of them were found in good accord with known experimental results. Astonishing agreement was obtained for alternant hydrocarbons. Several authors[5-11] have paid attention to this peculiar fact, and tried to see if there may be any correlations between the two antagonistic theories. It seems, however, that there are available no successful attempts that have made clear under what condition the two theories should become equivalent to each other. In the present paper a mathematical proof will be given for this problem. It will be shown that the static theory becomes equivalent to the localization theory, in case a certain condition is fulfilled. In fact, the latter condition is satisfied in many alternant hydrocarbons.

Terminology and Basic Relations

The LCAO molecular orbital (MO) method[3] in its simplest form is employed. Resonance integrals between non-adjacent atomic orbitals (AO) and overlap integrals are not considered here.

Symbols used in the present and subsequent papers in this series are given below.

n=number of AO's.

r, s, t, v, w=atoms of a conjugated system.

χ_r=AO for atom r.

ϕ_j=jth MO.

c_{jr}=coefficient of χ_r in ϕ_j.

ε=energy of a MO.

β_{rs}=resonance integral between atoms r, s.

α_r=coulomb integral of atom r.

E=total energy of π-electrons.

q_r=π-electron density at atom r.

p_{rs}=π-bond order of bond rs.

N_r=bond number at atom r.

F_r=free valence at carbon atom r.

$\pi_{r,r}$=self-polarizability of atom r.

$D(\varepsilon)$=secular determinant for a conjugated molecule, regarded as a function of ε.

$D_{r,s}(\varepsilon)$=determinant obtained by striking out the rth row and sth column of $D(\varepsilon)$.

$E_N^{(r)}$, $E_E^{(r)}$, $E_R^{(r)}$=total π-electron energies of the residual molecules[5] in nucleophilic, electrophilic and radical substitutions at carbon atom r.

$L_N^{(r)}$, $L_E^{(r)}$, $L_R^{(r)}$=localization energies in nucleophilic, electrophilic and radical substitutions at carbon atom r.

The prime after the symbol of summation denotes that the sum is taken only for the atoms adjacent to a given atom; e.g. for $\sum_s{}' p_{rs}$ the sum refers to atoms s adjacent to atom r.

The symbol to which a small zero is affixed, e.g. p_{rs}^0, E_0, refers to the initial state of a molecule, unless otherwise stated.

Every determinant occurring in an integral with respect to y is to be taken as a function of iy, where i is the imaginary unit, $\sqrt{-1}$.

The resonance integral between two adjacent carbon atoms of any molecule in its initial state is assumed to have a constant value β, which is negative. The energy of a MO and the coulomb integral of any atom are measured relative to the coulomb integral for carbon atom.

The general theory of molecular orbitals includes the following basic relations.

$$\int \phi_j \phi_k d\tau = \sum_{r=1}^{n} c_{jr} c_{kr} = \delta_{jk}, \tag{1}$$

$$N_r = \sum_s{}' p_{rs}, \tag{2}$$

$$F_r = \sqrt{3} - N_r, \tag{3}$$

$$E = \sum_{r=1}^{n} q_r \alpha_r + 2 \sum_{r>s}\sum p_{rs}\beta_{rs}, \tag{4}$$

$$q_r = \frac{\partial E}{\partial \alpha_r}, \tag{5}$$

$$2p_{rs} = \frac{\partial E}{\partial \beta_{rs}}, \tag{6}$$

$$\pi_{r,r} = \frac{\partial q_r}{\partial \alpha_r} = \frac{\partial^2 E}{\partial \alpha_r^2} < 0, \tag{7}$$

$$0 \leqq q_r \leqq 2, \tag{8}$$

$$L_N^{(r)} = E_N^{(r)} - E_0,\ L_E^{(r)} = E_E^{(r)} - E_0,$$

$$L_R^{(r)} = E_R^{(r)} - E_0. \tag{9}$$

All compounds treated in this study are even alternant hydrocarbons (AH). For

---

6) R. Daudel, C. Sandorfy, C. Vroelant, P. Yvan and O. Chalvet, *Bull. Soc. Chim. France*, **17**, 66 (1950).

7) F. H. Burkitt, C. A. Coulson and H. C. Longuet-Higgins, *Trans. Faraday Soc.*, **47**, 553 (1951).

8) H. H. Greenwood, *Trans. Faraday Soc.*, **48**, 585 (1952).

9) M. J. S. Dewar, *J. Am. Chem. Soc.*, **74**, 3355 (1952).

10) B. Pullman and A. Pullman, " Les théorie électroniques de la chimie organique ", Masson et Cie (1952), chapitre X.

11) K. Higasi, *Monogr. Res. Inst. Appl. Elec.*, **4**, 27 (1954).

such molecules the additional equations (10)-(12) hold:

$$q_r^0=1, \tag{10}$$

$$E_N^{(r)}=E_E^{(r)}=E_R^{(r)}, \tag{11}$$

$$L_N^{(r)}=L_E^{(r)}=L_R^{(r)}=L^{(r)}. \tag{12}$$

The quantities associated with the static and localization theories will be termed "static" and "dynamic", respectively.

Change in Total Energy of π-Electrons with Variation of Coulomb Integral

The fundamental equation[3)] in the treatment of ionic substitutions by the static theory is as follows:

$$\delta E=q_r^0\delta\alpha_r+\frac{1}{2}\pi_{r,r}^0\delta\alpha_r^2+\cdots\cdots, \tag{13}$$

where $\delta\alpha_r$ is assumed to be small in magnitude. Its sign is positive for a nucleophilic reagent and negative for an electrophilic one. Since in an AH, with which we are concerned, the initial electron density q_r^0 is 1 irrespective of r (see Eq. (10)), the difference in reactivity at its various positions is determined by the second term $\frac{1}{2}\pi_{r,r}^0\delta\alpha_r^2$.

Now, suppose that the coulomb integral of atom r changes from its initial value $\alpha_r^0=0$ to α_r which can be of any value from $-\infty$ to $+\infty$, and that the other coulomb and resonance integrals are throughout kept constant at their initial values. Then, instead of Eq. (13), the change in total energy will be given by

$$\varDelta E_r(\alpha_r)=E_r(\alpha_r)-E_0=\int_0^{\alpha_r}\frac{dE_r(\alpha_r)}{d\alpha_r}\,d\alpha_r, \tag{14}$$

which, from Eq. (5), may be written as

$$\varDelta E_r(\alpha_r)=\int_0^{\alpha_r}q_r(\alpha_r)\,d\alpha_r. \tag{15}$$

In the following some relations between α_r and $q_r(\alpha_r)$ will be described. First, it is easily seen that

$$\lim_{\alpha_r\to+\infty}q_r(\alpha_r)=0, \tag{16}$$

$$\lim_{\alpha_r\to-\infty}q_r(\alpha_r)=2. \tag{17}$$

From relation (7) it follows that, when α_r changes from $-\infty$ to $+\infty$, $q_r(\alpha_r)$ decreases monotonously from 2 to 0. According to the integral expression given by Coulson and Longuet-Higgins[3)]

$$q_r(\alpha_r)=1-\frac{1}{\pi}\int_{-\infty}^{\infty}\frac{D_{r,r}(iy)}{D(iy)}\,dy. \tag{18}$$

This reduces to

$$q_r(\alpha_r)=1-\frac{\alpha_r}{\pi}\int_{-\infty}^{\infty}\frac{-(D_{r,r}^0)^2}{(D^0)^2-\alpha_r^2(D_{r,r}^0)^2}\,dy, \tag{19}$$

since $D_{r,r}=D_{r,r}^0$, $D=D^0+\alpha_rD_{r,r}^0$, and D^0 and $D_{r,r}^0$ are even and odd functions of y, respectively[3)]. Therefore

$$q_r(-\alpha_r)-1=-\{q_r(\alpha_r)-1\}; \tag{20}$$

namely, the point, where $\alpha_r=0$ and $q_r=1$ is situated at the center of symmetry of the $q_r(\alpha_r)$ curve. This will be clear at a glance at the curve of Fig. 1, which was obtained by numerical calculations for benzene.

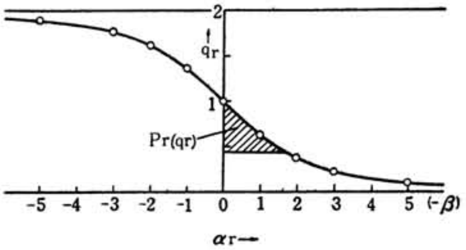


Fig. 1. $q_r(\alpha_r)$ for benzene.

Returning to Eq. (15), it will be seen that $\varDelta E_r(\alpha_r)$ is equal to the area under the curve between $\alpha_r=0$ and $\alpha_r=\alpha_r$. Consequently, from Eq. (20)

$$\varDelta E_r(\alpha_r)=\varDelta E_r(-\alpha_r)+2\alpha_r. \tag{21}$$

Since $D=D^0+\alpha\,D_{r,r}^0$ it is easily seen that, when $\alpha_r\to+\infty$ or $-\infty$, one of the solutions of the secular equation $D=0$ reduces to α_r, and the others to the solutions of $D_{r,r}^0=0$. $D_{r,r}^0=0$ is identical with the secular equation for the residual molecule. Hence it is verified that

$$\lim_{\alpha_r\to+\infty}\varDelta E_r(\alpha_r)=L_N^{(r)} \tag{22}$$

and

$$\lim_{\alpha_r\to-\infty}\{\varDelta E_r(\alpha_r)-2\alpha_r\}=L_E^{(r)}. \tag{23}$$

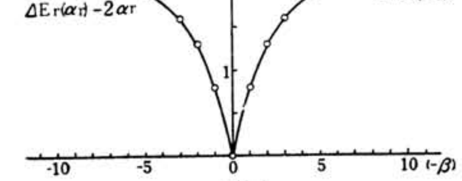


Fig. 2. $\varDelta E_r(\alpha_r)$ and $\varDelta E_r(\alpha_r)-2\alpha_r$ for benzene.

From Eqs. (21), (22) and (23) it follows that $L_N^{(r)}=L_E^{(r)}$. This is a well-known relation already cited as Eq. (12). Eqs. (21), (22) and (23) will be illustrated by an example shown in Fig. 2, where $\Delta E_r(\alpha_r)$ and $\Delta E_r(\alpha_r)-2\alpha_r$ for benzene are given.

Definition of Partial Polarization Energy

To begin with, a new quantity will be introduced. In the previous section the π-electron density at atom r was defined as a function of α_r, which was expressed as $q_r(\alpha_r)$. Conversely let α_r be regarded as a function of q_r and be written $\alpha_r(q_r)$. Since $q_r(\alpha_r)$ is a single-valued, continuous and monotonous function of α_r, $\alpha_r(q_r)$ is also such a function of q_r.

Consider a function of q_r as follows:

$$P_r(q_r)=\Delta E_r(\alpha_r(q_r))-q_r\alpha_r(q_r). \qquad (24)$$

Taking into account the definition of $\Delta E_r(\alpha_r)$ it is easily seen that $P_r(q_r)$ is equal to the area hatched in Fig. 1. Then $P_r(q_r)$ is expressed in an alternative form:

$$P_r(q_r)=-\int_{q_r^0}^{q_r}\alpha_r(q_r)\,dq_r. \qquad (25)$$

From Eqs. (14) and (24) it follows that

$$P_r(q_r)=E_r^*(q_r)-E_0, \qquad (26)$$

where

$$E_r^*(q_r)=E_r(\alpha_r(q_r))-q_r\alpha_r(q_r). \qquad (27)$$

Since it has been assumed that coulomb integrals except for α_r and resonance integrals are all kept at their initial values,

$$E_r(\alpha_r(q_r))=q_r\alpha_r(q_r)+2\sum_{v}\sum_{w}p_{vw}\beta \qquad (28)$$

(cf. Eq. (4)), where p_{vw} is the π-bond order of bond vw corresponding to $\alpha_r(q_r)$. So

$$E_r^*(q_r)=2\sum_{v}\sum_{w}p_{vw}\beta. \qquad (29)$$

Consider now the following conditions: (1) all the coulomb and resonance integrals, including α_r, should be invariant, i.e. they have the same values with those at the initial state of the molecule; (2) the coefficients of AO's should satisfy Eq. (1). Under these two conditions, the lowest value of the total energy of π-electrons is, of course, E_0, and the π-electron density at atom r is q_r^0 $(=1)$. On the other hand, if the former value were calculated under the same conditions with an additional one, i.e. (3) the π-electron density at atom r should be of a given value $q_r(\neq q_r^0)$, then it would become identical with $E_r^*(q_r)$. Consequently it is seen that

$$\left.\begin{array}{l} E_r^*(q_r)=E_0 \text{ and } P_r(q_r)=0 \ (q_r=q_r^0), \\ E_r^*(q_r)>E_0 \text{ and } P_r(q_r)>0 \ (q_r\neq q_r^0). \end{array}\right\} \qquad (30)$$

In short, $P_r(q_r)$ corresponds to the increment of the total energy due to the variation of π-electron density of atom r from its normal value $q_r^0=1$ to an imaginary one $q_r\neq q_r^0$. Then $P_r(q_r)$ might be called the partial polarization energy for atom r.

It follows from Eq. (20) that

$$P_r(q_r)=P_r(2-q_r), \qquad (31)$$

and by considering Eqs. (16) and (17) it is verified that

$$\lim_{q_r\to 0}E_r^*(q_r)=E_N^{(r)},\ \lim_{q_r\to 0}P_r(q_r)=L_N^{(r)}, \qquad (32)$$

$$\lim_{q_r\to 2}E_r^*(q_r)=E_E^{(r)},\ \lim_{q_r\to 2}P_r(q_r)=L_E^{(r)}. \qquad (33)$$

Therefore

$$L_N^{(r)}=P_r(0)=P_r(2)=L_E^{(r)}. \qquad (34)$$

This is again in accord with Eq. (12).

By differentiating Eq. (25)

$$\frac{dP_r(q_r)}{dq_r}=-\alpha_r(q_r), \qquad (35)$$

$$\frac{d^2P_r(q_r)}{dq_r^2}=-\frac{1}{\pi_{r,r}}>0. \qquad (36)$$

In Fig. 3 the relation between q_r and P_r is shown for benzene. It is to be noted that $dP_r(q_r)/dq_r=0$ at $q_r=q_r^0$ and that $|\pi_{r,r}^0|$ is equal to the radius of the curvature of the curve at $q_r=q_r^0$.

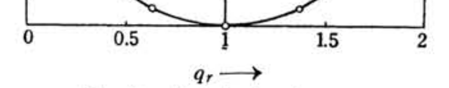


Fig. 3. $P_r(q_r)$ for benzene.

Correlation between the Two Sets of Quantities

Let us now consider the correlation between the static and dynamic quantities. It is well known that for an even AH

$D^0(\varepsilon)$ and $D^0_{r,r}(\varepsilon)$ are of the forms[3]:

$$D^0(\varepsilon)=\varepsilon^n-a_{n-2}\beta^2\varepsilon^{n-2}+a_{n-4}\beta^4\varepsilon^{n-4}-\cdots\cdots+(-1)^{n/2}a_0\beta^n, \qquad (37)$$

$$D^0_{r,r}(\varepsilon)=-\varepsilon^{n-1}+a^{(r)}_{n-3}\beta^2\varepsilon^{n-3}-a^{(r)}_{n-5}\beta^4\varepsilon^{n-5}+\cdots\cdots+(-1)^{n/2}a^{(r)}_1\beta^{n-2}\varepsilon, \qquad (38)$$

where

$$a_l\geqq 0 \quad (l=0,2,\cdots\cdots,n-2), \qquad (37')$$

$$a^{(r)}_l\geqq 0 \quad (l=1,3,\cdots\cdots,n-3). \qquad (38')$$

That is, the signs are alternately positive and negative, and $D^0(\varepsilon)$ has only even powers of ε, while $D^0_{r,r}(\varepsilon)$ only odd powers. From Eqs. (37) and (38) it follows that

$$D^0(iy)=(-1)^{n/2}(y^n+a_{n-2}\beta^2y^{n-2}+a_{n-4}\beta^4y^{n-4}+\cdots\cdots+a_0\beta^n), \qquad (39)$$

$$D^0_{r,r}(iy)=(-1)^{n/2}iy(y^{n-2}+a^{(r)}_{n-3}\beta^2y^{n-4}+a^{(r)}_{n-5}\beta^4y^{n-6}+\cdots\cdots+a^{(r)}_1\beta^{n-2}). \qquad (40)$$

Now consider two positions r and s in an even AH, and suppose that

$$a^{(r)}_l\geqq a^{(s)}_l \text{ for } l=1,3,\cdots\cdots,n-3, \qquad (41)$$

where $a^{(r)}_l$, $a^{(s)}_l$ are the coefficients of ε^l appearing in the expansions of $D^0_{r,r}$ and $D^0_{s,s}$, respectively. Throughout the following discussions it is assumed that for at least one value of l the inequality in (41) holds. Then, from Eq. (40), we have

$$\frac{D^0_{r,r}(iy)}{(-1)^{n/2}iy}>\frac{D^0_{s,s}(iy)}{(-1)^{n/2}iy}>0 \text{ for } -\infty<y<+\infty. \qquad (42)^*$$

As will be shown later, the relation (41) is valid in many conjugated molecules, e.g., for positions 1 and 2 in naphthalene:

$$\left.\begin{aligned} D^0_{1,1}(\varepsilon)&=-\varepsilon^9+9\beta^2\varepsilon^7-26\beta^4\varepsilon^5+29\beta^6\varepsilon^3-11\beta^8\varepsilon,\\ D^0_{2,2}(\varepsilon)&=-\varepsilon^9+9\beta^2\varepsilon^7-25\beta^4\varepsilon^5+26\beta^6\varepsilon^3-8\beta^8\varepsilon. \end{aligned}\right\} \qquad (43)$$

The integral expression given by Coulson and Longuet-Higgins[3] for the self-polarizability of atom r is

$$\pi^0_{r,r}=\frac{1}{\pi}\int_{-\infty}^{\infty}\left\{\frac{D^0_{r,r}(iy)}{D^0(iy)}\right\}^2dy, \qquad (44)$$

and the integral expression for $q_r(\alpha_r)$ has been already indicated as Eq. (19). If relation (41) is valid, then relation (42) will hold, so that

$$\{D^0_{r,r}(iy)\}^2<\{D^0_{s,s}(iy)\}^2<0 \quad (-\infty<y<\infty), \qquad (45)$$

except for $y=0$, where both terms are equal to zero. Then, considering the fact that $D^0(iy)$ is real for any value of y (cf. Eq. (39)), it follows that

$$\left.\begin{aligned} &\pi^0_{r,r}<\pi^0_{s,s}<0,\\ \text{or}\quad &|\pi^0_{r,r}|>|\pi^0_{s,s}|>0. \end{aligned}\right\} \qquad (46)$$

Further, under the above condition, it is evident that, when $\alpha_r=\alpha_s$,

$$\frac{-\{D^0_{r,r}(iy)\}^2}{\{D^0(iy)\}^2-\alpha_r^2\{D^0_{r,r}(iy)\}^2}>\frac{-\{D^0_{s,s}(iy)\}^2}{\{D^0(iy)\}^2-\alpha_s^2\{D^0_{ss,}(iy)\}^2}>0 \quad (-\infty<y<\infty,\ y\neq 0). \qquad (47)$$

Consequently, we have

$$\left.\begin{aligned} q_r(\alpha_r)<q_s(\alpha_s)<1 \quad (\alpha_r=\alpha_s>0),\\ q_r(\alpha_r)>q_s(\alpha_s)>1 \quad (\alpha_r=\alpha_s<0), \end{aligned}\right\} \qquad (48)$$

which are illustrated in Fig. 4. Hence, according to the definitions of $\Delta E_r(\alpha_r)$ and $P_r(q_r)$, it can be easily shown that

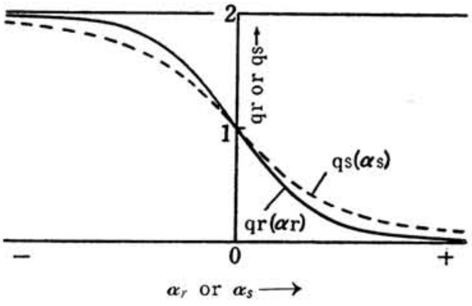


Fig. 4

$$\left.\begin{aligned} &\Delta E_r(\alpha_r)<\Delta E_s(\alpha_s) \qquad (\alpha_r=\alpha_s>0),\\ &\Delta E_r(\alpha_r)-2\alpha_r<\Delta E_s(\alpha_s)-2\alpha_s\\ &\qquad(\alpha_r=\alpha_s<0), \end{aligned}\right\} \qquad (49)$$

and

$$P_r(q_r)<P_s(q_s) \qquad (q_r=q_s\neq 1). \qquad (50)$$

Therefore, from Eqs. (21), (22) and (23) or from Eq. (34)

$$L^{(r)}_N=L^{(r)}_E<L^{(s)}_N=L^{(s)}_E. \qquad (51)$$

These situations are explained by Figs. 5 and 6. From Eqs. (36) and (46), it is seen that at $q_r=q_s=1$ the curvature of the curve $P_r(q_r)$ in Fig. 6 is smaller than that of the curve $P_s(q_s)$.

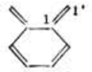
---

* If $a^{(r)}_1=a^{(s)}_1=0$, both the first and second symbols of inequality, and if $a^{(r)}_1=a^{(s)}_1>0$, the first symbol should be replaced by symbols of equality at $y=0$. But these corrections will cause no change to occur in the later results.

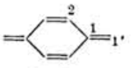
TABLE I

Compound	Position* r	$a_l^{(r)}$						$\pi^0_{r,r}$ $(1/\beta)$	F^0_r	$L^{(r)}$ $(-\beta)$
		$l=11$	9	7	5	3	1			
Butadiene	1						2	0.626(a)	0.838(e)	1.644(k)
	2						1	0.402(a)	0.391(e)	2.472(k)
Hexatriene	1					4	3	0.685(a)	0.861(e)	1.524(k)
	3					3	2	0.470(a)	0.464(e)	2.160(k)
	2					3	1	0.389(a)	0.378(e)	2.516(k)
Octatetraene	1				6	10	4		0.870(e)	1.463(k)
	3				5	7	3		0.479(e)	2.080(k)
	4				5	7	2		0.445(e)	2.217(k)
	2				5	6	1		0.375(e)	2.530(k)
Decapentaene	1			8	21	20	5		0.874(e)	1.426(k)
	3			7	16	14	4		0.485(e)	1.999(k)
	5			7	16	13	3		0.458(e)	2.117(k)
	4			7	16	13	2		0.441(e)	2.237(k)
	2			7	15	10	1		0.374(e)	2.536(k)
Benzene						4	3	0.398(a)	0.399(e)	2.536(k)
Naphthalene	1			9	26	29	11	0.443(a)	0.452(f)	2.299
	2			9	25	26	8	0.405(a)	0.404(f)	2.480
	9			8	21	20	5	0.330(a)	0.104(f)	3.056
Anthracene	9	14	74	188	245	158	40	0.526(b)	0.520(g)	2.01 (k)
	1	14	73	181	224	129	26	0.454(b)	0.459(g)	2.25 (k)
	2	14	72	173	203	107	18	0.411(b)	0.408(g)	2.40 (k)
Phenanthrene	1	14	73	182	228	135	29	0.439(b)	0.452(g)	2.30 (k)
	9	14	73	181	227	137	31	0.442(b)	0.451(g)	2.30 (k)
	4	14	73	181	224	129	26	0.429(b)	0.440(g)	2.39 (k)
	3	14	72	174	208	116	24	0.407(b)	0.407(g)	2.41 (k)
	2	14	72	174	207	113	21	0·403(b)	0.404(g)	2.50 (k)
Diphenyl	2		11	43	74	56	15	0.423(c)	0.436(g)	2.400(c)
	4		11	42	70	53	15	0.411(c)	0.412(g)	2.447(c)
	3		11	42	69	49	12	0.396(c)	0.395(g)	2.544(c)
	1		10	36	58	43	12		0.124(g)	2.919(k)
Styrene	β				7	13	7		0.821(h)	1.704(h)
	2				6	10	4		0.443(h)	2.370(h)
	α				6	9	4		0.415(h)	2.424(h)
	4				6	9	4		0.415(h)	2.424(h)
	3				6	9	3		0.395(h)	2.546(h)
	1				5	7	3		0.106(g)	2.960(k)
o-Quinodimethane	1′				7	13	7		0.957(i)	1.23 (k)
	1				5	6	1		0.094(i)	2.96 (k)
p-Quinodimethane	1′				7	13	7		0.974(i)	1.21 (k)
	2				6	9	2		0.462(i)	2.21 (k)
	1				5	5	1		0.070(i)	3.02 (k)
Diphenylene	1		12	48	80	53	9	0.419(d)	0.428(j)	2.408(d)
	2		12	47	77	53	12	0.443(d)	0.421(j)	2.352(d)

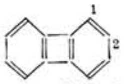
* The numbering of positions is given as follows:



for *o*-quinodimethane,



for *p*-quinodimethane,



for diphenylene.

For the other molecules the numbering system of Chemical Abstracts has been employed.

(a) From reference 3.
(b) H. C. Longuet-Higgins and C. A. Coulson, *J. Chem. Soc.*, **1949**, 971.
(c) R. D. Brown, *Experientia*, **6**, 376 (1950).
(d) R. D. Brown, *Trans. Faraday Soc.*, **46**, 146 (1950).
(e) C. A. Coulson, *Proc. Roy, Soc.*, **A169**, 413 (1939).
(f) J. E. Lennard-Jones and C. A. Coulson, *Trans. Faraday Soc.*, **35**, 811 (1939).
(g) R. D. Brown, *Aust. J. Sci. Res.*, A, **2**, 564 (1949).
(h) R. D. Brown, *J. Am. Chem. Soc.*, **75**, 4077 (1953).
(i) A. Pullman, G. Berthier and B. Pullman, *Bull. Soc. Chim. France*, **15**, 450 (1948).
(j) R. D. Brown, *Trans. Faraday Soc.*, **45**, 296 (1949).
(k) From Table I of reference 7.

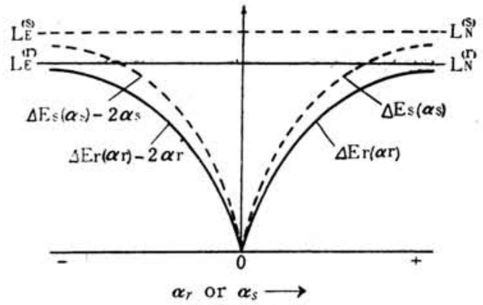


Fig. 5

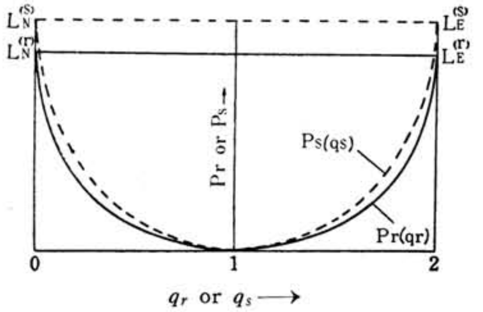


Fig. 6

Thus it has been strictly proved that, when the condition of inequalities (41) holds, the self-polarizability of atom r becomes larger in magnitude than that of atom s, and the localization energy for atom r becomes smaller than that of atom s. That is, if the relation (41) can be found for any two atoms r and s in a given molecule, whether we employ the static theory or the localization one, we necessarily reach the same conclusion that atom r is more reactive than atom s in both electrophilic and nucleophilic substitutions. Regarding naphthalene, for instance, the static and localization theories should give the same prediction that the position 1 is more reactive than position 2 (cf. Eqs. (43)). The values of $a_i^{(r)}$, $\pi_{r,r}^0$, F_r^0 and $L^{(r)}$ for various even AH's are summarized in Table I.

Discussion

In studying the relationship between the static and dynamic quantities, it is highly important to note that the self-polarizability $\pi_{r,r}^0$ for atom r, which is a static quantity, is closely related to the determinant $D_{r,r}^0$ (cf. Eq. (44)), which is the very secular determinant for the residual molecule at the transition state. This fact may suggest that some correlation between the two sets of quantities, $\pi_{r,r}^0$ and $L^{(r)}$ $(=L_N^{(r)}=L_E^{(r)})$, should be found in the property of the determinant $D_{r,r}^0$ itself. It is not unnatural, if we be led to the inequalities (41).

For every pair of positions in molecules treated in Table I this condition of inequalities is satisfied. There are only a few cases of exception, viz. positions 1 and 9 in phenanthrene and 1 and 2 in diphenylene. The sequences found in the magnitudes of both the static and dynamic quantities are also in accord with what should be expected from our preceding arguments. However, for positions 1 and 9 in phenanthrene the results of the two theories do not agree with each other. It is to be noted here that inequalities (41) are a sufficient but not necessary condition, and therefore even if the inequalities do not hold, it should not always lead to the conclusion that the static and localization theories give contradictory predictions concerning the reactivity of positions r and s. This is the reason why the predictions of the two theories for positions 1 and 2 in diphenylene do not contradict each other.

Next, we shall proceed to the discussion of the quantity $P_r(q_r)$ that has been defined as the partial polarization energy. In the localization theory it is assumed that, in the transition state, 0 or 2 π-electrons are held fixed on the carbon atom attacked according as the reagent is nucleophilic or electrophilic, respectively. As described previously this assumption of complete localization (or polarization) is obviously an extreme one, and it might be more plausible to consider that there should occur partial localization (or polarization) of π-electrons at the transition state. Remember that we have defined the partial polarization energy P_r as a function of q_r which can take any value between 0 and 2. Then we may preferably employ $P_r(q_r)$, instead of the localization energy $L_N^{(r)}$ or $L_E^{(r)}$, as the measure of the reactivity in the ionic substitutions.

In general, it is difficult to estimate to what extent the polarization of the electrons will take place at the transition state. Fortunately, however, when inequalities (41) hold for two positions r and s in an alternant hydrocarbon, $P_r(q_r)$ will be less than $P_s(q_s)$ for any value of $q_r=q_s$ (see Eq. (50)). In such a case, therefore, from the viewpoint of partial polarization the conclusion will be reached that atom r is more reactive than atom s both in nucleophilic and electrophilic substitutions.

As is seen from Eq. (36) the quantity $P_r(q_r)$ is also related to static quantity $\pi^0_{r,r}$ at $q_r=q^0_r$. We can thus say that the partial polarization energy $P_r(q_r)$ is a quantity of a more general nature which can represent the static and dynamic quantities at some special values of q_r.

A similar situation will arise with the quantity $\Delta E_r(\alpha_r)$ or $\Delta E_r(\alpha_r)-2\alpha_r$. Indeed, $\Delta E_r(\alpha_r)$ defined by Eq. (14) is more general than δE of Eq. (13), since the latter is the same as $\Delta E_r(\delta\alpha_r)$.

In the discussion of the relationship between the static and dynamic quantities, Brown[5] has derived a rule of chemical non-crossing which is in good agreement with the trends in curves of Fig. 6 or Fig. 5.

Only alternant hydrocarbons have been treated in this study. In a non-alternant hydrocarbon or a molecule containing hetero atoms, such a relation as inequalities (48) does not necessarily hold, because the π-electron densities q^0_r and q^0_s are in general not equal to each other. Therefore it cannot be expected that the two theories should always give the identical prediction for the reactivity of positions r and s, either for nucleophilic or electrophilic reagents.

Summary

A mathematical proof is given that under a certain condition the static and localization theories become completely equivalent to each other in predicting the reactivities in ionic substitutions of the positions in a given even alternant hydrocarbon. The said condition is concerned with the coefficients of the powers in the expansions of the secular determinants for the residual molecules. It is shown by numerical calculations that the condition is fulfilled by almost all positions in 12 molecules treated. The change in total energy of π-electrons is given as a function of a coulomb integral, and a new quantity called partial polarization energy is introduced which is defined as a function of the π-electron density at a given position. Both are useful for relating the static quantity to the dynamic one. The latter is a new measure of a general nature for the reactivity of the position towards the ionic reagents.

The author wishes to express his sincere thanks to Professor K. Higasi for his guidance and encouragement throughout the present work. Thanks are also due to Professor K. Fukui and Dr. S. Nagakura for valuable criticism. He is indebted to the Ministry of Education for a grant-in-aid.

Research Institute of Applied Electricity
Hokkaido University, Sapporo