442. *Charge-transfer Complexes and the Mechanism of Aromatic Substitution. Part II.*[1] *Molecular-orbital Calculations.*

By R. D. Brown.

A simple molecular-orbital treatment of the mechanism of aromatic substitution developed in Part I leads to quantities termed Z-values as indices of chemical reactivities of positions in aromatic compounds. The calculations of Z-values depend upon two parameters which characterize the nature of the electrophil and the transition state in reaction. These parameters have been evaluated for nitration at 0° in acetic anhydride. The resultant Z-values for positions in polycyclic hydrocarbons show a good linear correlation with logarithms of rates of nitration, the correlation being superior to that shown by atom-localization energies or superdelocalizabilities. The orientation of substitution in some non-benzenoid hydrocarbons is also accounted for satisfactorily by Z-values. Although it is possible to calculate Z-values when charge transfer from more than one occupied orbital of the aromatic compound is considered, orbitals other than the frontier orbital scarcely alter the Z-value except when the orbital is almost degenerate with the frontier orbital.

The effect of inductive substituents on the Z-values of benzene positions is evaluated by first-order perturbation theory. The results are in agreement with observed orientations of substitution for such benzene derivatives. The quantitative selectivity relationships for electrophils observed by H. C. Brown and Nelson are explained by the present theory which predicts that the same quantitative relation should hold for all purely inductively substituted benzenes. Some calculations of Z-values for benzenes with conjugating substituents are reported. They account for the general features of orientation of substitution in these compounds.

Calculations of the extent of charge transfer in the transition state for the complexes formed in the nitration of polycyclic hydrocarbons show that it is virtually complete except in the case of benzene.

The significance of frontier-electron densities, superdelocalizabilities, π-electron densities, and atom-localization energies in the light of the charge-transfer mechanism of aromatic substitution is discussed.

In Part I[1] a new mechanism was proposed for aromatic substitution, involving the formation of unsymmetrical charge-transfer complexes between the electrophil E^+ and the

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[1] Part I, R. D. Brown, preceding paper.

aromatic compound ArH. It was possible to formulate the activation energy for formation of such complexes by using a " configuration interaction " molecular-orbital method. In the present paper it is proposed to show that a quantitative treatment of relative reactivities of different aromatic compounds, or different positions in an aromatic compound, is possible. Because of the large body of numerical data now available in the literature the simple molecular-orbital treatment is a convenient basis for the calculations.

It was shown in Part I that the activation energy for formation of the charge-transfer complex is

$$\Delta E^{\ddagger} = X^{\ddagger} + Y^{\ddagger} - W^{0} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where $X^{\ddagger} = H_{00}{}^{\ddagger} - E^{0}$, E^{0} being the energy of the separated reactants and $H_{00}{}^{\ddagger}$ the energy value for the configuration $E^{+} \ldots ArH$ with the geometry of the transition state. W^{0} is the most positive solution of a secular equation and if we consider charge transfer from the highest filled molecular orbital of ArH only then

$$W^{0} = \tfrac{1}{2}\{\Delta^{\ddagger} + (\Delta^{\ddagger 2} + H_{01}{}^{\ddagger 2})^{\frac{1}{2}}\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

or, for $\Delta^{\ddagger 2} \gg H_{01}{}^{\ddagger 2}$

$$W^{0} = \Delta^{\ddagger} + H_{01}{}^{\ddagger 2}/\Delta^{\ddagger} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where

$$\Delta^{\ddagger} = A^{\ddagger} - I \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$A^{\ddagger}$ being the effective electron affinity of the electrophil when desolvated to the extent appropriate to the transition state, and I the ionisation potential of the aromatic compound. $H_{01}{}^{\ddagger}$ is the resonance integral for interaction of the singlet configurations $\Psi_0 = E^{+} \ldots ArH$ and $\Psi_1 = E \ldots ArH^{+}$ in the transition state:

$$H_{01}{}^{\ddagger} = \int \Psi_0{}^{\ddagger} \mathscr{H}^{\ddagger} \Psi_1{}^{\ddagger} d\tau \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The configurations are represented more explicitly by antisymmetrized products of orbital functions, or linear combinations of these:

$$\Psi_0 = \mathscr{A}[\psi_1(1)\alpha(1)\psi_1(2)\beta(2) \ldots \psi_f(n-1)\alpha(n-1)\psi_f(n)\beta(n)]$$

$$\Psi_1 = \frac{1}{\sqrt{2}}\{\mathscr{A}[\psi_1(1)\alpha(1)\psi_1(2)\beta(2) \ldots \psi_f(n-1)\alpha(n-1)\chi_e(n)\beta(n)] \\ + \mathscr{A}[\psi_1(1)\alpha(1)\psi_1(2)\beta(2) \ldots \chi_e(n-1)\alpha(n-1)\psi_f(n)\beta(n)]\}$$

where $\mathscr{A}$ is the antisymmetrizer operator, ψ_f the frontier molecular orbital of the aromatic compound and χ_e the lowest energy vacant orbital of the electrophil.* To proceed further we shall take the Hamiltonian operator to be

$$\mathscr{H}^{\ddagger} = \sum_{i} \mathbf{H}_{\text{eff}}{}^{\ddagger}(i) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where $\mathbf{H}_{\text{eff}}{}^{\ddagger}(i)$ is a Hartree–Fock one-electron Hamiltonian operator, the summation being over all electrons sufficiently loosely bound for their transfer to the vacant electrophil orbital to be taken into consideration. In the calculations described below the transfer of an electron from some or all of the π-molecular orbitals has been considered (although the inclusion in the calculations of configurations arising from transfer from any but the highest two or three π-orbitals was found to have a negligible effect) but transfer from the σ-orbitals was neglected. Terms in the total Hamiltonian applying to electrons too firmly bound to the aromatic compound for transfer to be significant make no contribution to the

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* It is assumed here that χ_e is an atomic orbital but for some electrophils it might be a more extensive molecular orbital. This makes no significant difference to our analysis [the constant $c_{f\mu}$ in eqn. (7) must then be taken to be the product of the frontier-orbital coefficient of χ_μ and the coefficient of that atomic orbital in χ_e which overlaps X_μ] so long as χ_e appreciably overlaps only one of the $2p\pi$ orbitals of the aromatic system. For some reagents such as ozone, dienophils, etc., multiple overlapping may be an important feature in any " charge-transfer complex " mechanism for their attack on conjugated systems.

expression for the energy of formation of the complex when the approximations described below are introduced and so have not been included in (6).

To make the calculations more manageable and to put them on a footing comparable with previous molecular-orbital treatments of chemical reactivity, the simple Hückel LCAO approximation will be invoked—the two-electron integrals occurring in the evaluation of $H_{01}^{\ddagger}$ will be neglected, it being supposed that compensation for this is achieved by empirical evaluation of one-electron integrals (the coulomb and resonance parameters of the Hückel method). The molecular orbitals of the aromatic compound will be taken to be linear combinations of $2p\pi$-atomic orbitals and overlap integrals will be neglected.

The configuration-interaction integral then reduces to

$$\begin{aligned} H_{01}^{\ddagger} &= \sqrt{2}c_{f\mu}\int\chi_e\mathbf{H}_{\text{eff}}^{\ddagger}\chi_\mu d\tau \\ &= \sqrt{2}c_{f\mu}\beta_{e\mu} \quad \ldots\ldots\ldots\ldots \quad (7) \end{aligned}$$

$C_{f\mu}$ being the coefficient of χ_μ in the frontier orbital of ArH, χ_μ being the $2p\pi$-orbital overlapped appreciably by the electrophil orbital. The resonance integral $\beta_{e\mu}$ represents the interaction energy of the electrophil orbital χ_e and the $2p\pi$-orbital of ArH which it overlaps. It will be assumed that for a given electrophil $\beta_{e\mu}$ has the same value for any carbon atom μ whose substitution is under consideration. This is virtually equivalent to assuming that for a given electrophil the distance between it and the carbon atom to which it attaches itself is constant in all activated complexes.*

It is convenient to express $\beta_{e\mu}$ in terms of β, the standard resonance integral of a benzene bond:

$$\beta_{e\mu} = g_e^{\ddagger}\beta \quad \ldots\ldots\ldots\ldots \quad (8)$$

$g_e^{\ddagger}$ being a constant characteristic of the particular electrophil under consideration.

If charge transfer from orbitals other than the frontier orbital is considered the configuration-interaction treatment of the activation energy involves matrix elements of the type $H_{0j}^{\ddagger}$ and $H_{jk}^{\ddagger}$. These have the values:

$$\begin{aligned} H_{0j}^{\ddagger} &= \sqrt{2}g_e c^{\ddagger}_{j\mu}\beta \\ H_{jk}^{\ddagger} &= -\int\psi_j\mathbf{H}_{\text{eff}}^{\ddagger}\psi_k d\tau = 0 \end{aligned}$$

The value of W^0 in equation (1) then becomes the most positive zero of the function

$$f(W) = \left(W - 2g_e^{\ddagger 2}\beta^2\sum_j\frac{c_{j\mu}^2}{W - \Delta_j^{\ddagger}}\right)\Pi_k(W - \Delta_k^{\ddagger}) \quad \ldots\ldots \quad (9)$$

It remains to express $\Delta_j^{\ddagger}$ in terms of the Hückel MO treatment of the system. The ionization potential for the jth molecular orbital of ArH is written $-e_j = -\alpha - y_j\beta$, α being the standard Coulomb integral of carbon, y_j a number calculated from the Hückel secular equations. The electron affinity of the vacant orbital χ_e of the electrophil may be written $A^{\ddagger} = -\alpha - y_e^{\ddagger}\beta$, $y_e^{\ddagger}$ being a number characteristic of the particular electrophil considered.

Then

$$\begin{aligned} \Delta_j^{\ddagger} &= A^{\ddagger} - I_j \\ &= -\beta(y_e^{\ddagger} - y_j) \quad \ldots\ldots\ldots\ldots \quad (10) \\ &= -\beta Y_j\text{, say,} \quad \ldots\ldots\ldots\ldots \quad (11) \end{aligned}$$

where Y_j is a number, positive if $\Delta_j^{\ddagger}$ is positive. As pointed out in Part I, $\Delta_f^{\ddagger}$ is positive, *i.e.*, Y_f is positive, when electrophilic substitution occurs.

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* This distance will be determined by two factors: Non-bonded repulsions will tend to keep the electrophil and the aromatic compound from approaching one another too closely but, subject to this, the more extensively χ_e and χ_μ overlap, the more stable the complex will be.

If (11) is substituted in (9) and we write $W = -\beta Z$ then the value of W^0 is obtained from the most positive zero of the function

$$F(Z) = \left(Z - 2g_e^{\ddagger 2}\sum_j \frac{c_{j\mu}^2}{Z - Y_j}\right)\Pi_k(Z - Y_k) \quad . \quad . \quad . \quad . \quad . \quad (12)$$

Equations (2) and (3) similarly simplify to

$$Z^0 = -W^0/\beta = [Y + (Y^2 + 2g_e^{\ddagger 2}c_\mu^2)^{\frac{1}{2}}]/2 \quad . \quad . \quad . \quad . \quad (13)$$

and

$$Z^0 = Y + 2g_e^{\ddagger 2}c_\mu^2/Y \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

the quantities Y and c_μ^2 referring to the highest filled orbital (frontier orbital) of the aromatic compound.

Nitration of Polycyclic Aromatic Hydrocarbons.—The success with which the present theory accounts for relative rates of electrophilic substitution reactions may be judged from the recently determined data [2] for nitration of polycyclic aromatic hydrocarbons. Nitration is a suitable reaction because it has been shown that the formation of a charge-transfer complex is the rate-determining step, at least for hydrocarbons which are not too reactive. Suitable values of the parameters $g_e^\ddagger$ [equation (8)] and $y_e^\ddagger$ [equation (10)], characterizing the transition state and the electrophil in this reaction, were first determined by trial and error. The value of $y_e^\ddagger$ would be expected to be greater than y_j for the frontier orbital of benzene, *i.e.*, greater than unity, and $g_e^\ddagger$ to be less than unity. The values $y_e^\ddagger = 2$, $g_e^\ddagger = 0{\cdot}6_1$ were found to be appropriate (these may not be the optimum values but $y_e^\ddagger$ is probably within $\pm 0{\cdot}5$ and g_e within $\pm 0{\cdot}1$ of the optimum values). Values of Z^0 calculated by using these values and equation (13), for the hydrocarbons studied by Dewar, Warford, and Mole,[2] and including charge-transfer from the frontier orbitals only, are listed in Table 1. To examine the effect of including charge transfer from the next-to-frontier orbitals equation (12) was solved and the resultant values are also listed in Table 1. It will be seen that the inclusion of the second occupied orbitals in the calculation scarcely affects the Z value in most cases. The extent to which the Z-values, calculated with two occupied orbitals included, correlate with experimental reaction rate constants is shown in Fig. 1. The success of this correlation provides support for the assumptions made in setting up the present theory (*e.g.*, the assumption that $X^\ddagger$ is independent of the nature of ArH); assumptions of this general type have of course been made in previous molecular-orbital theories of chemical reactivity.

The success of the correlation also implies that variations in rates of nitration can be ascribed primarily to variations in $\Delta E^\ddagger$, $\Delta S^\ddagger$ remaining constant or varying in proportion to variations in $\Delta E^\ddagger$.

Previously molecular-orbital treatments of electrophilic substitution have been based on calculations of π-electron densities, atom-localization energies or superdelocalizabilities;[3,4] for alternant hydrocarbons only the last two vary from one position to another. For comparison with Z-numbers the superdelocalizabilities have been computed for the positions studied experimentally; first-order approximations to atom-localization energies (the " reactivity-numbers " of Dewar) are already available.[2] The numerical values are given in Table 1 and the extent to which they correlate with the observed rates may be judged from Figs. 2 and 3. It is evident that Z-numbers show a better linear correlation with the logarithms of rates than do other theoretical quantities. With the exception of the points for triphenylene which lie well off the lines in all correlations and for which we can offer no theoretical explanation, all rates may be predicted from Z-values to better than a factor of 2 although the total range is more than 1 : 10^5.

Dewar, Mole, and Warford have attributed most of the scatter of the points on Fig. 2 to steric effects. If the rate-determining step is the formation of a charge-transfer complex

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[2] Dewar, Mole, and Warford, *J.*, 1956, 3581.

[3] Fukui, Yonezawa, and Nagata, *Bull. Chem. Soc. Japan*, 1954, **27**, 423.

[4] Fukui, Yonezawa, and Nagata, *J. Chem. Phys.*, 1957, **27**, 1247.

of the geometry envisaged in Part I, with the electrophil situated above the attacked carbon atom (aromatic plane horizontal) and the C–H bond scarcely stretched then the steric hindrance even at positions like the 4-position in phenanthrene would not be very great. It would be only when an adjacent carbon atom had a bulky substituent attached, or when a large electrophil was involved, that significant steric effects would be expected. However most of the small scatter of points in Fig. 1 could be attributed to small steric effects, although other factors, not primarily connected with π-electrons, such as variation in $\Delta S^{\ddagger}$ owing to differing extents of " solvent-freezing," etc., could equally be responsible.

FIG. 1. *Z-Values plotted as a function of rates of nitration of polycyclic hydrocarbons.*

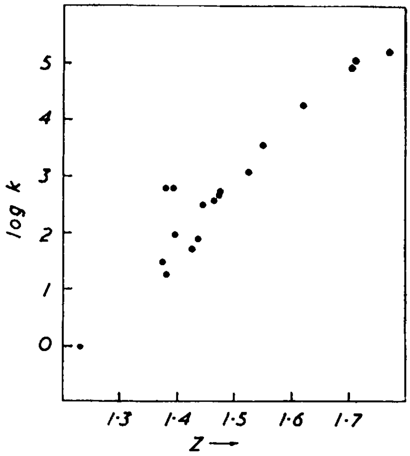
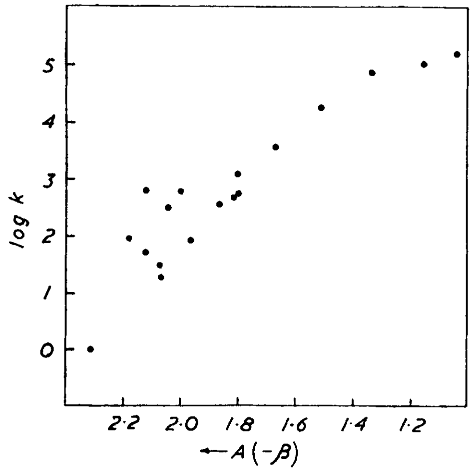


FIG. 2. *Atom-localization energies as a function of rates of nitration.*



Orientation of Substitution in Conjugated Hydrocarbons.—The Z-values for various positions in a conjugated hydrocarbon are determined primarily by Y_f and c_f^2, the lower filled orbitals making little contribution except when one of them is nearly degenerate with the frontier orbital. Thus the relative reactivities of different positions in a conjugated system are indicated by the values of c_f^2, *i.e.*, by the frontier electron density.[3] This explains the success of the frontier electron density method of accounting for orientation of substitution, and why frontier electron densities nevertheless do not indicate the relative reactivities of two positions in *different* conjugated systems. Such an explanation of the significance of frontier electron densities had previously been lacking. Fukui *et al.*[3] have suggested that reactivities should be characterized by superdelocalizabilities and the frontier electron densities make a major contribution to these but the proportional contributions from other occupied orbitals to superdelocalizabilities are considerably greater than to Z-values.

It has already been shown [5] that frontier electron densities satisfactorily account for the orientation of substituents in alternant hydrocarbons; Z values will likewise be in agreement with observed orientations for such compounds. To demonstrate further the agreement between orientations predicted by Z-values and observed orientations, the positions of highest Z-value for some non-benzenoid hydrocarbons and the observed orientations are given in Table 2. Charge transfer from the two highest-energy occupied orbitals of the hydrocarbons was included and parameters appropriate for nitration were used. The position preferentially attacked by electrophils is known in all cases except that of pleiadiene. In each case the position attacked is that of highest Z-value. The case of fluoranthene is of interest because the calculated π-electron densities [6] are greater

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[5] Fukui, Yonezawa, and Shinger, *J. Chem. Phys.*, 1952, **20**, 722.

[6] " Dictionary of Values of Molecular Constants," edited by C. A. Coulson and R. Daudel, Centre national de la Recherche scientifique, Paris, 1955, Vol. III, Part I, p. 14.

than unity at the 2- and the 8-position, less than unity at the 1- and the 3-position yet, as correctly predicted by *Z*-values, it is the 3-position which is preferentially nitrated.[7]

Although pleiadiene has been nitrated[8] the position of attack has not yet been established. From calculated *Z*-values it is predicted to be the 3-position (contrast π-electron density data[9] which show the 1-position to have the highest reactivity) and the magnitude of *Z* indicates extraordinarily high reactivity.* In such circumstances the nitronium ion might be expected to show little discrimination between the various positions of the hydrocarbon. To examine this point theoretically the *Z*-values of all positions were computed, including *all* occupied orbitals in the calculation because even small

TABLE 1.

Compound	Posn.	log *k* *	*Z* (*a*)	*Z* (*b*)	*A* †	*S* ‡	*T* §
Benzene		0	1·207	1·223	2·31	0·833	0·75
Diphenyl	2	1·48	1·345	1·373	2·07	0·910	0·960
	4	1·26	1·381	1·381	2·07	0·894	0·929
Naphthalene	1	2·67	1·474	1·474	1·81	0·994	0·929
	2	1·70	1·419	1·427	2·12	0·873	0·973
Phenanthrene	1	2·56	1·455	1·465	1·86	0·977	0·955
	2	1·96	1·396	1·397	2·18	0·860	0·999
	3	2·48	1·447	1·447	2·04	0·893	0·962
	4	1·90	1·424	1·437	1·96	0·939	0·979
	9	2·69	1·482	1·483	1·80	0·997	0·934
Pyrene	1	4·23	1·618	1·620	1·51	1·115	0·958
Triphenylene	1	2·78	1·377	1·393	2·00	0·888	0·952
	2	2·78	1·377	1·381	2·12	0·928	0·952
Chrysene	2	3·54	1·552	1·552	1·67	1·044	0·949
Perylene	3	4·89	1·700	1·705	1·34	1·195	0·970
Benzopyrene	6	5·03	1·712	1·712	1·15	1·408	0·947
Coronene		3·06	1·517	1·525	1·80	0·991	0·960
Anthanthrene	6	5·19	1·769	1·771	1·03	1·504	0·964

(*a*) Considering charge transfer from frontier orbital only. (*b*) Including frontier and next highest filled orbital.

* Relative rates of nitration (see ref. 10).

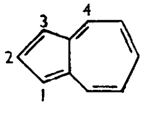
† Atom localization energies estimated by first order perturbation theory (see ref. 10).

‡ Superdelocalizabilities (see ref. 4).

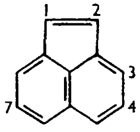
§ Extent of charge transfer in the transition state [see equation (19)].

TABLE 2.

Hydrocarbon	Posn.	*Z*	Most active posn.	Hydrocarbon	Posn.	*Z*	Most active posn.
Azulene (I)	1	1·663	1	Fluoranthene (IV)	3	1·454	3
Acenaphthylene (II)	1	1·505	1	Diphenylene (V)	2	1·598	2
Pleiadiene (III)	3	1·821	?				



(I)



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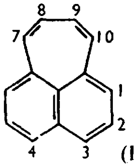

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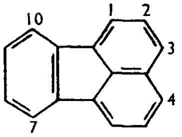

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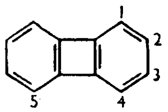

(V)

TABLE 3. *Z-Values for pleiadiene, all occupied orbitals included.*

Posn.	*Z*	Posn.	*Z*
1	1·824	7	1·808
2	1·763	8	1·792
3	1·832		

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* For compounds of such high reactivity the formation of the charge-transfer complex may no longer be rate-determining (see Part I).

[7] von Braun and Manz, *Annalen*, 1931, **488**, 111; 1932, **496**, 170.

[8] Boekelheide and Vick, *J. Amer. Chem. Soc.*, 1956, **78**, 653.

[9] Pullman, Pullman, Berthier, and Pontis, *J. Chim. phys.*, 1952, **49**, 20.

contributions from lower orbitals might alter the order of Z-values. The results are given in Table 3. It seems likely that both the 1- and the 3-nitro-derivatives would be formed in appreciable amounts judging from the Z-values.

Electrophilic Substitution in Benzene Derivatives: Inductive Effect only.—As a further test of the proposed molecular-orbital treatment of chemical reactivity let us consider the inductive effect of substituents on the Z-numbers for benzene. In the molecular-orbital theory the inductive effect amounts to a perturbation to the Coulomb integral of the carbon atom to which the substituent is attached. Let the change in the Coulomb integral be $h\beta$. This perturbation splits the degeneracy of the frontier orbitals of benzene, the energy of only one orbital being changed to the first order in h. The perturbations to the orbital energies and coefficients are conveniently obtained by the method of Bassett and Brown:[10]

FIG. 3. *Superdelocalizabilities as a function of rates of nitration.*

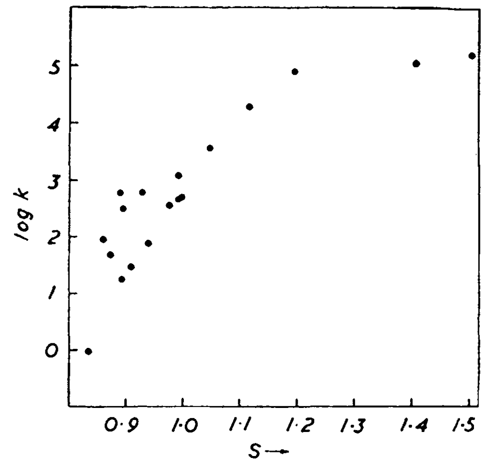
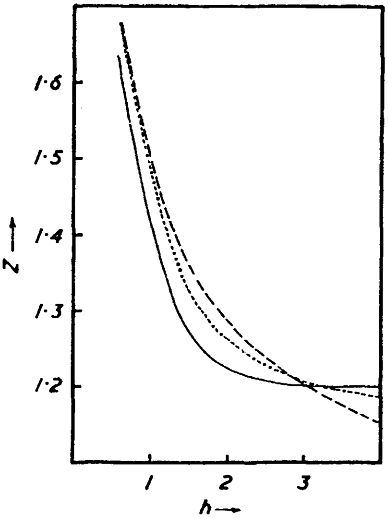


FIG. 4. *Z-Values for* Ph·X.



. . . *ortho*, —— *meta*, – – – *para*.
$k = 0{\cdot}8,\ h^{(1)} = 0{\cdot}1h$.

Unperturbed orbital: $y_f = 1,\ c_o^2 = 1/4,\ c_m^2 = 1/4,\ c_p^2 = 0$.

Perturbed orbital: $y_{f-1} = 1 + h/3,\quad c_o^2 = 1/12 - 11h/108;\quad c_m^2 = 1/12 + 7h/108;\quad c_p^2 = 1/3 + 4h/108$.

The change in the Z-value for benzene caused by this perturbation may be derived by a first-order perturbation treatment of equation (12). It is:

$$\delta Z = 2g_e^{\ddagger 2}\sum_j \frac{c_j^2\delta Y_j + (Z_b - Y_j)\delta c_j^2}{(Z_b - Y_j)^2}\left\{1 + 2g_e^{\ddagger 2}\sum_k \frac{c_k^2}{(Z_b - Y_k)^2}\right\}^{-1} \quad . \quad . \quad (15)$$

where Z_b is the Z-value of unperturbed benzene and the summations are over all occupied orbitals, or over those orbitals from which charge transfer is considered. If we consider only the frontier orbitals of benzene and use the values of parameters found appropriate for nitration at 0° (see above) as typical values, then $Z_b = 1{\cdot}207$ and we find:

Position	*ortho*	*meta*	*para*
δZ	$-0{\cdot}125h$	$-0{\cdot}037h$	$-0{\cdot}265h$

These values are in harmony with the accepted properties of inductively substituted benzenes. For $-I$ substituents (h positive) the Z-values require *meta*-substitution with deactivation (Z less than Z_b). For $+I$ substituents (*e.g.*, alkylbenzenes) the Z-values require *ortho–para*-substitution with activation.

[10] Bassett and R. D. Brown, *Proc. Phys. Soc.*, 1958, *A*, **71**, 724.

The results for positive h also are appropriate for pyridine in which *meta*-substitution with deactivation occurs.

It has often been assumed that inductive effects fall off along a chain of atoms in geometric progression.[11] To allow for this in the molecular-orbital treatment auxiliary inductive parameters $h^{(1)}$, $h^{(2)}, \ldots$ are included such that for an atom separated from the centre of perturbation by $n - 1$ atoms, the Coulomb integral is increased by $h^{(n)}\beta$ with $h^{(n)} = \theta^n h$, θ being a number such that $0 < \theta < 1$. Properties of aliphatic compounds suggest the value [11] $\theta = \frac{1}{3}$. Although until recently there was no strong evidence from the *chemical reactivities* of conjugated systems that it was necessary to include such auxiliary parameters, SCF[12] and SCE [13,14] calculations show that parameters of this type should be included in the simple MO calculations. However the origin of these auxiliary inductive effects may be traced to penetration integral effects so that they are not directly comparable to the inductive effects observed in saturated compounds and the value $\theta = \frac{1}{3}$ is therefore not necessarily the appropriate one (it is not certain yet that the geometric progression formula is apposite). The perturbation calculations have therefore been performed by using general values of $h^{(n)}$. The relevant orbital data are:

$$\delta y_f = (1/2)h^{(1)} + (1/2)h^{(2)};\ \delta y_{f-1} = (1/3)h^{(0)} + (1/6)h^{(1)} + (1/6)h^{(2)} + (1/3)h^{(3)}$$

Position	$\delta c_f{}^2$	$\delta c_{f-1}{}^2$
ortho	$(1/8)h^{(1)} - (1/8)h^{(2)}$	$(1/216)(-22h^{(0)} - 5h^{(1)} + 13h^{(2)} + 14h^{(3)})$
meta	$-(1/8)h^{(1)} + (1/8)h^{(2)}$	$(1/216)(14h^{(0)} + 13h^{(1)} - 5h^{(2)} - 22h^{(3)})$
para	0	$(1/216)(8h^{(0)} + 28h^{(1)} - 44h^{(2)} + 8h^{(3)})$

and, for the values of parameters appropriate for the nitration reaction

Position	δZ
ortho	$-[0{\cdot}125h^{(0)} + 0{\cdot}302h^{(1)} + 0{\cdot}390h^{(2)} + 0{\cdot}037h^{(3)}]$
meta	$-[0{\cdot}037h^{(0)} + 0{\cdot}390h^{(1)} + 0{\cdot}302h^{(2)} + 0{\cdot}125h^{(3)}]$
para	$-[0{\cdot}265h^{(0)} + 0{\cdot}074h^{(1)} + 0{\cdot}250h^{(2)} + 0{\cdot}265h^{(3)}]$

To determine the effect of including charge transfer from the remaining occupied orbital of benzene also, the perturbation calculations were repeated with this extension. The relevant data for the lowest filled orbital are:

$$\delta y_{f-2} = (1/6)h^{(0)} + (1/3)h^{(1)} + (1/3)h^{(2)} + (1/6)h^{(3)}$$

Position	$\delta c_{f-2}{}^2$
ortho	$(1/216)[5h^{(0)} + 22h^{(1)} - 14h^{(2)} - 13h^{(3)}]$
meta	$(1/216)[-13h^{(0)} - 14h^{(1)} + 22h^{(2)} + 5h^{(3)}]$
para	$(1/216)[-19h^{(0)} - 26h^{(1)} + 10h^{(2)} + 35h^{(3)}]$

With the values of parameters appropriate for nitration (Z_b now is 1·223) we find

	δZ
ortho	$-[0{\cdot}125h^{(0)} + 0{\cdot}282h^{(1)} + 0{\cdot}390h^{(2)} + 0{\cdot}041h^{(3)}]$
meta	$-[0{\cdot}041h^{(0)} + 0{\cdot}390h^{(1)} + 0{\cdot}282h^{(2)} + 0{\cdot}125h^{(3)}]$
para	$-[0{\cdot}265h^{(0)} + 0{\cdot}083h^{(1)} + 0{\cdot}249h^{(2)} + 0{\cdot}240h^{(3)}]$

As was found when considering the nitration of polycyclic hydrocarbons the inclusion of the lower orbital in the calculations has only a small effect on the calculated Z-values.

Selectivity of Electrophils.—The concept of selectivity of electrophils—that the more reactive the electrophil the less discriminating it is in selecting the site of substitution—was put on a quantitative footing by H. C. Brown and Nelson [15] who considered partial rate factors for substitution in toluene. Calling the common logarithm of the ratio of partial rate factors for the *para* and a *meta* position the selectivity factor F_s, they found

$$\log p_f = AF_s \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

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[11] Dewar, *J.*, 1949, 463.

[12] R. D. Brown and Heffernan, *Austral. J. Chem.*, 1957, **10**, 211.

[13] R. D. Brown and Heffernan, *Trans. Faraday Soc.*, 1958, **54**, 757.

[14] R. D. Brown and Heffernan, results in course of publication.

[15] H. C. Brown and Nelson, *J. Amer. Chem. Soc.*, 1953, **75**, 6292.

the constant A being independent of the electrophil and having the value 1·3. The present molecular-orbital treatment provides a quantitative theoretical basis for this relationship. In terms of Z-values we have

$$\log p_f = -\frac{\beta}{2{\cdot}303\boldsymbol{R}T}(Z_p - Z_b)$$

and

$$F_s = -\frac{\beta}{2{\cdot}303\boldsymbol{R}T}(Z_p - Z_m)$$

Thus the constant A in (16) becomes

$$A = (Z_p - Z_b)/(Z_p - Z_m).$$

It now has to be shown that A is independent of the nature of the electrophil in the case of an inductively substituted benzene such as toluene. For such benzene derivatives the perturbation treatment given above may be used. For benzene the expression in braces in (15) has the same value for all positions and so

$$A = \sum_j \frac{c_{jp}{}^2\delta Y_j + (Z_b - Y_j)\delta c_{jp}{}^2}{(Z_b - Y_j)^2}\left\{\sum_k \frac{(c_{kp}{}^2 - c_{km}{}^2)\delta Y_k + (Z_b - Y_k)(\delta c_{kp}{}^2 - \delta c_{km}{}^2)}{(Z_b - Y_k)^2}\right\}^{-1} \quad (17)$$

It has been seen that the inclusion of the lowest occupied orbital in the calculation has little effect; if it is omitted then (17) can be simplified, remembering that $Y_f = Y_{f-1}$:

$$A = \frac{\frac{1}{3}\delta Y_{f-1} + (Z_b - Y_f)\delta c_{f-1,p}{}^2}{\frac{1}{4}\delta Y_{f-1} - \frac{1}{4}\delta Y_f + (Z_b - Y_f)(\delta c_{f-1,p}{}^2 - \delta c_{f,m}{}^2 - \delta c_{f-1,m}{}^2)}$$

If we include only the primary inductive parameter $h^{(0)}$, and use equation (14) to estimate $Z_b - Y_f = 2g_e{}^{\ddagger 2}/3Y_f$, we find:

$$A = \frac{36 - 8g_e{}^{\ddagger 2}/Y_f}{27 + 6g_e{}^2/Y_f} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

For small values of $g_e{}^{\ddagger 2}/Y_f$, A is independent of the nature of the electrophil, its value being 1·3 which is fortuitously in excellent agreement with the experimental value. For nitration $g_e{}^{\ddagger 2}/Y_f = 0{\cdot}75$ and the value of this ratio would not be expected to vary greatly from this value, especially as both $g_e{}^{\ddagger}$ and Y_f would be expected to increase with increasing reactivity of the electrophil. If the nitration values are used, then instead of the use of the approximate expression (18) A can be calculated directly from the perturbation theory results: $A = 0{\cdot}265/(0{\cdot}265 - 0{\cdot}041) = 1{\cdot}2$ when charge transfer from all orbitals is included and only the primary inductive parameter $h^{(0)}$ is used. The value is altered only slightly when auxiliary inductive parameters are included.

Thus on the assumption that the ratio $g_e{}^{\ddagger}/Y_f$ for benzene does not vary too greatly with the nature of the electrophil, the present theory accounts for H. C. Brown and Nelson's observations on selectivity relationships for electrophils and requires only the use of perturbation theory.

The present treatment of the selectivity factors implies that the value of A should be independent of the nature of the *substrate* provided that this is an inductively substituted benzene. This conclusion is borne out by published diagrams[16] of log p_f *versus* F_s for various substrates. Those with purely inductive substituents have gradients indistinguishable from that for toluene although substrates with conjugating substituents show large variations in gradient.

Benzene Substituents with both Mesomeric and Inductive Effects.—To examine the ability of the present theory to account for electrophilic substitution in substituted benzenes in which the substituent exerts both a mesomeric and an inductive effect, calculations of Z-values have been performed for the conjugated system (VI), X being characterized by a

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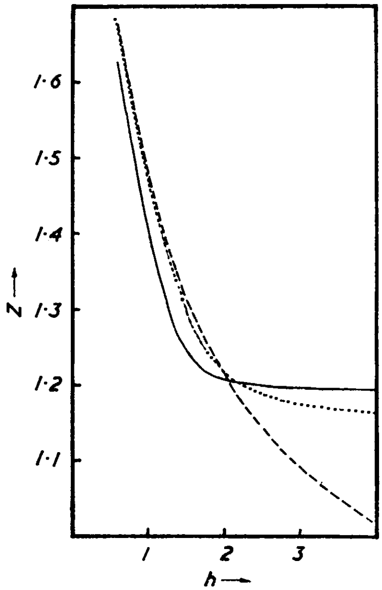
[16] Nelson, *J. Org. Chem.*, 1956, **21**, 145.

Coulomb integral $h\beta$ relative to carbon, by a resonance integral $\beta_{cx} = k\beta$, and by an inductive Coulomb integral $h^{(1)}\beta$ for the carbon atom to which X is attached. Representative calculations for values of h, k, and $h^{(1)}$ which are likely to be appropriate for substituents such as halogen, OH, or NH_2, are summarized in Figs. 4, 5, and 6.

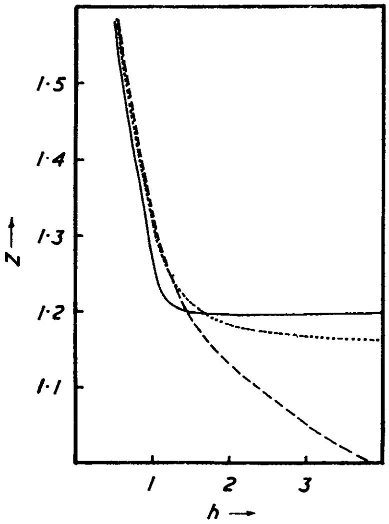
The results are in agreement with the main features of substitutions observed in this kind of benzene derivative—*ortho-para*-substitution with the overall level of reactivity of the molecule decreasing as the electronegativity of the substituent increases. The relative separations of the curves for the three positions are seen to depend particularly on the magnitude of the auxiliary inductive parameter (and this would be influenced by inclusion of further inductive parameters as in the geometric-progression formula mentioned above), and to some extent on the degree of conjugation of the substituent with the ring (*i.e.*, or the value of k). In due course it is intended to study more fully the variation of Z-values with the values of the molecular-orbital parameters of the substituent to attempt to account in more detail for observed variations in rates of nitration of benzene derivatives.

FIG. 5. *Z-Values for* Ph·X.



. . . *ortho*, — *meta*, – – – *para*.
$k = 0{\cdot}8$, $h^{(1)} = 0{\cdot}25h$.

FIG. 6. *Z-Values for* Ph·X.



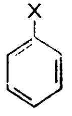
. . . *ortho*, —— *meta*, – – – *para*.
$k = 0{\cdot}5$, $h^{(1)} = 0{\cdot}25h$.

Extent of Charge Transfer.—In Part I the approximate formula $T = 1 - (H_{01}{}^{\ddagger}/\Delta^{\ddagger})^2$ was derived for the extent of charge transfer in the transition state for formation of the initial complex. If equations (7) and (11) are substituted in this expression we have

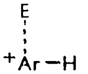
$$T \approx 1 - 2g_e{}^{\ddagger 2}c_f{}^2/Y_f{}^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

Values of T derived from (19) are given in Table 1. In all cases except that of benzene, charge transfer is substantially complete, indicating that the formula (VII) used in Part I to represent charge-transfer complexes is an acceptable one, at least in the case of the complexes which intervene in the nitration of aromatic hydrocarbons.

The Significance of Other Molecular-orbital Quantities.—The significance of frontier electron densities in the light of the present mechanism of electrophilic substitution has been discussed above; they are expected to indicate the relative Z-values of different positions in the same molecule. Superdelocalizabilities were introduced as an approximate estimate of the variation in activation energy for the substitution reaction, the sp^3 configuration being assumed for the transition state. Although there is strong evidence that (VIII) is not the rate-determining transition state in nitration and bromination reactions but rather an unsymmetrical configuration somewhat like (VII) [see Part I], the theoretical treatment leading to the superdelocalizability concept could equally be applied to structures like (VII). Thus superdelocalizabilities are an alternative criterion of reactivity according to the present mechanism. We believe that they are less satisfactory than Z-values because of difficulties relating to the electronegativity of E and the extent of charge transfer. These difficulties were noticed by Fukui *et al.*,[4] but they were not able to devise a means of circumventing them for numerical work. The difficulties are avoided by the present configuration-interaction technique.



(VI)



(VII)

(VIII)

Previous treatments based on the transition state (VIII) coupled reactivity of a position with its π-electron density or its atom-localization energy, according to two alternative approximate views of the structure of (VIII).[17] This procedure has the disadvantage that the prediction of orientation in alternant hydrocarbons was based on localization energies, because all positions have the same π-electron density, yet when the orientations predicted by charge densities differ from those predicted by localization energies (as often happens for heterocyclic molecules) the experimental orientation almost always agrees with that predicted by π-electron densities, not by localization energies.* The present treatment is based on a single theoretical quantity—the Z number—and so this dilemma does not arise. It has the further advantage that the nature of the electrophil, and the possibility that different electrophils may yield differing relative reactivities for a series of aromatic compounds, are explicitly recognized in the theory. This more comprehensive viewpoint is achieved at the cost of introducing two parameters, $y_e^\ddagger$ and $g_e^\ddagger$, characteristic of the electrophil, which for the present must be evaluated empirically.

By using valence-bond terminology the present approach may be compared more pictorially with the π-electron density and delocalization energy methods. When the π-electron density is used as a criterion of reactivity this is equivalent to viewing the structure of the transition state as $E^+ \ldots ArH$, the bonding between the reactants being purely ionic. When localization energies are used it amounts to assuming the structure of the transition state to be $E{-}ArH^+$ with a pure covalent bond between the electrophil and the carbon atom undergoing substitution, the bond being strong enough to eliminate this carbon from the conjugated system. In the present charge-transfer configuration approach the structure of the transition state is regarded as predominantly corresponding to Ψ_1 with small contributions from Ψ_0 and other configurations. Now Ψ_1 is readily decomposed into

$$\sum_{\mu} c_{f\mu}\{\mathscr{A}[\psi_1(1)\alpha(1)\ldots\chi_\mu(n-1)\alpha(n-1)\chi_e(n)\beta(n)] + \mathscr{A}[\psi_1(1)\alpha(1)\ldots\chi_e(n-1)\alpha(n-1)\chi_\mu(n)\beta(n)]\}/\sqrt{2},$$

i.e., into a sum of configurations in which the electron transferred to the electrophil orbital is paired with the frontier-orbital electron, located in turn in each $2p\pi$-orbital of the conjugated system of ArH. Thus the transition state is viewed as predominantly a " resonance hybrid " of $E{-}ArH^+$ structures in which the bond links the electrophil in

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* Orientations in unreactive species such as protonated cations of heterocycles follow localization energies however.[18]

[17] R. D. Brown, *Quart. Rev.*, 1952, **6**, 63.

[18] R. D. Brown, " Current Trends in Heterocyclic Chemistry," Butterworths, London, 1958, p. 13.

turn to each carbon atom of the aromatic system, the bonds between the electrophil and every carbon atom except the μth being very long and energetically negligible; the relative weights of the structures are given by the frontier electron densities. A small contribution from Ψ_0, corresponding to $E^+ \ldots ArH$, and from other configurations which may be dissected as above, are also implied in the complete eigenfunction. In the charge-transfer approach the bond between the electrophil and the μth carbon atom is not strong enough to exclude the carbon atom from the conjugated system of the aromatic system although the extent of conjugation within the aromatic system (represented, say, by the sum of the bond orders) is reduced in the charge-transfer complex as compared with the original aromatic compound.

It has not been possible to demonstrate theoretically any analytical relationship between Z-numbers and π-electron densities, or between Z-numbers and localization energies. However qualitatively it seems reasonable that these quantities will be roughly related because presumably the transfer of charge from an aromatic compound to an electrophil would be easiest (energetically) from the position of highest charge in the aromatic system; and the original " isolated molecule " viewpoint [17] justifying the correlation of π-electron densities and chemical reactivity is equally applicable to the present mechanism of substitution. The Wheland localization-energy approach amounts to giving extreme importance to just one of the configurations which enter into the charge-transfer theory.

Distinction between π- and σ-Electrons.—The charge-transfer complexes are not planar molecules and so the symmetry distinction between π- and σ-electrons is lost. However the more important distinction between π- and σ-electrons is that the former are more loosely bound to the molecule then the latter, and the success of the " π-electron approximation," widely adopted in theoretical chemistry, in which detailed interactions and motions are considered for π-electrons only, the σ-electrons being treated as part of the core, seems to depend largely on the energy difference between σ- and π-electrons although the strict orthogonality between π- and σ-orbitals has certain useful consequences for establishing a partial variational theorem.[19]

If the energies of the π-electrons in ArH are not too greatly reduced when the charge-transfer complex is formed then there will be in the complex two groups of electrons of energies similar to the π- and σ-electrons in ArH and it seems convenient still to designate them as π- and σ-electrons for easy reference.*

In the charge-transfer complexes the bond between the electrophil and the aromatic compound is a " resonance hybrid " of a series of bonds involving each conjugated atom in ArH, all but one of these bonds being extremely weak, the strongest of them being about 0·6β (in the case of nitration complexes) and this having a weight in the " resonance hybrid " typically around 0·1 to 0·4. Thus the interaction is weak enough for the energy distinction between π- and σ-electrons still to apply.

However it may happen in some cases, possibly with " addition " reagents which have orbitals that appreciably overlap more than one of the aromatic compound and give addition reactions, that stronger interactions are involved, appreciably lowering the energies of the most loosely bound electrons so that their distinction from the σ-electrons is not so marked. It is hoped to take up this aspect further in a subsequent publication on addition reactions.

The author is grateful to Professor B. Pullman of the University of Paris for communicating eigenvectors and eigenvalues of anthanthrene, from which the reported Z-values of this molecule were computed, and to Mr. R. D. Harcourt who obtained eigenvectors and eigenvalues on the electronic computer CSIRAC from which the data in Figs. 4—6 were computed.

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* This represents a further generalization of the π–σ terminology, just as the currently accepted terminology is an extension of the original one applying to linear molecules only. .

[19] Lykos and Parr, *J. Chem. Phys.*, 1956, **24**, 1166.