A Theoretical Treatment of Molecular Complexes.
II. Iodine-Aromatic Hydrocarbon Complexes

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Theoretical and experimental research into the benzene-iodine complex has derived many welcome conclusions. With regard to the configuration of benzene-iodine complex for instance, Mulliken[1] had considered the symmetries of the molecular orbitals of electron donor and acceptor and predicted the resting model in which the iodine molecule is situated above the benzene molecule, with its axis parallel to the benzene plane and its center on the sixfold axis of the benzene molecule. This model, however, was contradictory to the

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

results of the study of X-ray diffraction[2] and of infrared spectra[3]. Both of these results supported the axial model in which the axis of iodine molecule was coincident with the sixfold axis of benzene. The reason for this discrepancy was pointed out by Aono[4], who calculated the magnitude of the overlap integral between a benzene molecule and an iodine molecule and made it clear that the error in the estimation of the overlap integral in Mulliken's treatment might be the reason for this discrepancy. Further, a numerical calculation for the benzene-iodine complex was made with respect to the axial model by using experimental data such as the ionization potential, so that a considerable agreement was found between the theoretical values and the experimental data of dipole moment, charge transfer spectra, and so on.

Another discrepancy between the theoretical and experimental data was found concering the intensity of the charge transfer spectra for the complex of iodine-benzene derivatives. From a theoretical point of view, the intensity of the charge transfer spectra would be expected to increase in proportion to the basicity of the aromatic molecule. On the other hand, experimental data showed the opposite[5]. In order to elucidate this experimental result the concept of the contact charge transfer spectra was introduced by Mulliken[6]. On the other hand, a statistical consideration of the configuration of aromatic compound-iodine complexs was made by Murakami, and numerical calculations of the intensity of the charge transfer spectra which were carried out on the basis of the statistical consideration showed a clear correlation with the experimental result[7].

It has recently been pointed out by many authors that the ease of complex formation depends not only on the charge transfer spectra, but also on the magnitude of other intermolecular interactions, such as dispersion force, exchange repulsion energy, and electrostatic force[6,7]. In many cases, the discussions of molecular complex formation in which these factors were taken into account seemed to be rather qualitative than quantitative. A more detailed discussion is in order.

In this paper we intend to apply aromatic hydrocarbon-iodine complex to the delocalization method that has already been used for aromatic compound-silver complexes[8], and to compare the results of numerical calculation with the experimental results, bearing the effects of the dispersion force in mind.

Model and Formulation

The procedure used in this paper is the same as has been described in a previous paper[8], that is, the delocalization method. In order to execute the theoretical treatment for aromatic compound-iodine complexes, the model adopted is the axial one in which the axis of the iodine molecule is coincident with the sixfold axis of one of the benzene rings in an aromatic compound; this model was supported by X-ray diffraction[3] as well as by infrared spectra[4] for benzene-iodine or benzene-bromine complexes.

In this model the stabilization energy due to the delocalization of π electrons from the aromatic compound to the iodine molecule is obtained by the perturbation method, in the same way as has been described in the previous paper.

Prior to the formulation, the electronic configuration of the iodine molecule should be discussed. The six outer-shell molecular orbitals of iodine molecule may approximately be written as a linear combination of two $5p_x$, $5p_y$ and $5p_z$ orbitals, as is shown in Eq. 1 (normalized factors are omitted).

$$\left.\begin{array}{ll} \phi_1 \approx 5p_x + 5p_x' & \phi_4 \approx 5p_y - 5p_y' \\ \phi_2 \approx 5p_y + 5p'_y & \phi_5 \approx 5p_z - 5p_z' \\ \phi_3 \approx 5p_z + 5p_z' & \phi_6 \approx 5p_x - 5p_x' \end{array}\right\} \qquad (1)$$

In which $5p_x$, $5p_y$ and $5p_z$ are the atomic orbitals of iodine atoms and the x axis is taken to be the molecular axis of the iodine molecule. Therefore, the orbital ϕ_1 is nothing but the σ-bonding orbital, and ϕ_6, the σ-antibonding orbital.

At the stage of the first approximation, only ϕ_1 and ϕ_6 are involved in the linear combination of the atomic orbital for the total system of the complex, and the conjugations between the aromatic compound and one of ϕ_2, ϕ_3, ϕ_4 and ϕ_5 are neglected since the magnitude of overlap integrals between the $5p_y$ as well as the $5p_z$ and $2p\pi$ atomic orbital in aromatic compounds may reasonably be expected to be much smaller than that between $5p_x$ and $2p\pi$ in the axial model.

The secular equation for this model is written in a simple LCAO MO treatment (overlap neglected) in the following form:

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2) E. E. Ferguson, *J. Chem. Phys.*, **25**, 577 (1956).

3) O. Hassel, *Molecular Phys.* **1**, 241 (1958).

4) S. Aono, *Progr. Theoret. Phys. Japan*, **22**, 313 (1959).

5) L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **74**, 4500 (1952).

6) R. S. Mulliken, *Rec. trav. chim.*, **75**, 845 (1956); L. E. Orgel and R. S. Mulliken, *J. Am. Chem. Soc.*, **79**, 4839 (1957).

7) H. Murakami, This Bulletin, **28**, 577 (1955), ibid., **28**, 581 (1955), *J. Chem. Phys.*, **23**, 1957 (1955).

8) K. Fukui, A. Imamura, T. Yonezawa and C. Nagata, This Bulletin, **34**, 1076 (1961).

$$D(\lambda)=$$

$$\begin{vmatrix} h-\lambda & l & 0\cdots & \cdots & \cdots & \cdots 0 \\ l & h-\lambda & \gamma\cdots\cdots & \gamma\ 0\cdots & \cdots & \cdots 0 \\ 0 & \gamma & a_{11}-\lambda & a_{12}\cdots\cdots & a_{16}\cdots\cdots & a_{1n} \\ \vdots & \vdots & a_{21} & a_{22}-\lambda\cdots & a_{26}\cdots\cdots & a_{2n} \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \vdots & \gamma & a_{61} & a_{62}\cdots\cdots & a_{66}-\lambda\cdots & a_{6n} \\ \vdots & 0 & \vdots & \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & a_{n1} & a_{n2}\cdots\cdots & a_{n6}\cdots\cdots & a_{nn}-\gamma \end{vmatrix}$$

$$=\{(h-\lambda)^2-l^2\}\Delta(\lambda) + (h-\lambda)\gamma^2\sum_{r,s=1}^{6}(-1)^{r+s+1}\Delta_{rs}(\lambda) \qquad (2)$$

in which

$$\Delta(\lambda)=\begin{vmatrix} a_{11}-\lambda & a_{12} & \cdots\cdots\cdots a_{1n} \\ a_{21} & a_{22}-\lambda & \cdots\cdots a_{2n} \\ \cdots\cdots & \cdots\cdots & \cdots\cdots \\ a_{n1} & a_{n2} & \cdots\cdots\cdots a_{nn}-\lambda \end{vmatrix} \qquad (3)$$

is the secular determinant for the isolated aromatic molecule and $\Delta_{rs}(\lambda)$ denotes the secular determinant with row r and column s struck out, and a_{ii} and $a_{ij}(i\neq j)$ are the Coulomb and the resonance integrals respectively; h and l are the Coulomb and the resonance integrals of 5p orbital in iodine molecule respectively, and γ is the resonance integral between the $2p\pi$ orbital of carbon atom in the aromatic compound and the $5p_x$ orbital of the iodine atom, which is the one of two iodine atoms nearer to the aromatic molecule. The suffixes $1, 2, 3\cdots\cdots, 6$ of the Coulomb and the resonance integrals in Eq. 2 correspond to the numbers of the constituent atoms of the benzene ring above which the iodine molecule is located.

Since the magnitude of γ is small, the perturbation method can be applied in this treatment, as has been shown in the previous paper.

Case 1: When neither $h+l$ nor $h-l$ is equal to any λ_j, the roots of Eq. 2, $\lambda^{(1)}, \lambda^{(2)}\cdots\cdots, \lambda^{(n)}$; $\lambda'^{(1)}$ and $\lambda'^{(2)}$ are represented by:

$$\lambda^{(j)}=\lambda_j+\frac{(\lambda_j-h)}{(\lambda_j-h)^2-l^2} \times(c_1{}^j+c_2{}^j+\cdots+c_6{}^j)^2\gamma^2+[\gamma^4] \quad (j=1, 2, \cdots, n) \qquad (4)$$

$$\lambda'^{(k)}=\lambda'_k+\frac{1}{2}\sum_{j=1}^{n}\frac{(c_1{}^j+c_2{}^j+\cdots\cdots+c_6{}^j)^2}{\lambda'_k-\lambda_j} \times\gamma^2+[\gamma^4] \quad (k=1,2)$$

in which λ_j is the root of $\Delta(\lambda)=0$, and λ_1' λ_2' are equal to $h+l$ and $h-l$ respectively; $c_r{}^j$ is the coefficient of the rth atomic orbital in the jth molecular orbital; and $[\gamma^4]$ denotes the higher term. The delocalization energy for complex formation that was defined for silver-aromatic hydrocarbon complexes in the previous paper[8] may be described for the iodine-aromatic molecular complex as follows:

$$\Delta E=\left\{\sum_{j=1}^{m}\frac{2(\lambda_j-h)}{(\lambda_j-h)^2-l^2}(c_1{}^j+c_2{}^j+\cdots-+c_6{}^j)^2 +\sum_{j=1}^{n}\frac{(c_1{}^j+c_2{}^j+\cdots\cdots+c_6{}^j)^2}{h+l-\lambda_j}\right\}\gamma^2+[\gamma^4] \qquad (5)$$

in which $\lambda_1, \lambda_2, \cdots\cdots, \lambda_m$ correspond to the occupied orbitals.

Case 2: When $h-l$ is equal to the highest occupied orbital, λ_m, of the isolated aromatic molecule, the roots of Eq. 2 are represented by:

$$\left.\begin{matrix}\lambda^{(m)}\\ \lambda'^{(2)}\end{matrix}\right\}=\lambda_m\pm\frac{1}{\sqrt{2}}|c_1{}^j+c_2{}^j+\cdots\cdots+c_6{}^j|\gamma+[\gamma^2]$$

$$\lambda^{(j)}=\lambda_j+\frac{(\lambda_j-h)}{(\lambda_j-h)^2-l^2}(c_1{}^j+c_2{}^j+\cdots\cdots+c_6{}^j)^2\gamma^2 +[\gamma_4] \quad (j=1,2,\cdots\cdots,n;\ j\neq m) \qquad (6)$$

$$\lambda'^{(1)}=\lambda_1'+\frac{1}{2}\sum_{j=1}^{n}\frac{(c_1{}^j+c_2{}^j+\cdots\cdots+c_6{}^j)^2}{\lambda_1'-\lambda_j}\gamma^2+[\gamma^4]$$

In presenting the value of energies, we make the zero point equal to the Coulomb integral of the benzene carbon atom and express them in units of $(-\beta)$, which is the resonance integral of the benzene C–C bond.

In both cases, 1 and 2, the formulas for the delocalization energy indicate that the magnitude of delocalization energy depends upon the symmetry of the benzene ring combined with the iodine molecule; this conclusion is quite coincident with that of Mulliken's theory. This circumstance is similar to the case of silver-aromatic hydrocarbon complexes, as has been pointed out in the previous paper[8].

Result and Discussion

Benzene-Iodine Complex.—With regard to the benzene-iodine complex, many theoretical and experimental studies had been carried out as has been described in the introduction. In this paper we carry out the numerical calculation for the comparison with the experimental data of benzene-iodine complex, making use of the delocalization method. For the charge transfer spectrum, the transition of the π electron may occur from the lowest occupied π orbital of benzene to the lowest vacant orbital of the iodine molecule, and the transition from the highest occupied π orbital of benzene to the lowest vacant orbital of iodine is forbidden for the sake of the symmetry of complex of the axial model. Accordingly, the frequency of the charge transfer spectrum is given by:

$$\boldsymbol{h}\nu=\left\{2+\frac{6(2-h)}{(2-h+l)(2-h-l)}\gamma^2\right\}-\left\{(h-l)+\frac{3}{h-l-2}\gamma^2\right\}+[\gamma^4] \qquad (7)$$

in which $\boldsymbol{h}$ is Planck's constant and ν is the charge transfer frequency, and the first term and the second term correspond to the energy of the lowest occupied π orbital of benzene and that of the lowest vacant orbital of iodine molecule respectively. The energy is represented in units of $(-\beta)$ in Eq. 7.

In order to determine the value of h, l and γ, we adopt the semi-empirical treatment, that is, the value of l and γ are obtained on the assumption that the resonance integral is proportional to the corresponding overlap integral, and h is determined bearing in mind the fact that the value of $h-l$ is nothing but the electron affinity of the iodine molecule. The values used in the calculation have been taken as follows after a consideration of many experimental data:

The resonance integral of the benzene C–C bond: 2.39 eV.[9]
The electron affinity of the iodine molecule: 7.0 eV.[10]
The distance of the iodine-iodine bond in iodine molecule: 2.67 Å
The distance between the nearer iodine atom and a carbon atom of the benzene ring in the axial model; 3.7 Å*

Adopting these parameters in calculation, we can get the values of h, l and γ as follows:

$$h=1.45 \qquad l=1.39 \qquad \gamma^2=0.021 \qquad (8)$$

The frequency of the charge transfer spectrum and the magnitude of dipole moment of this complex are calculated and listed in Table I in comparison with the experimental results.

TABLE I. FREQUENCY OF THE CHARGE TRANSFER SPECTRUM AND THE DIPOLE MOMENT OF BENZENE-IODINE COMPLEX

	Calcd.	Obs.
Dipole moment (Debye unit)	1.31	0.72
Charge transfer spectrum, cm^{-1}	37.1×10^3	36.5×10^3

The solvent effect is taken into account to compare the observed value of charge transfer spectrum with that calculated in Table I, that is, $36.5\times10^3\,\mathrm{cm}^{-1}$ in Table I is obtained by adding $2\times10^3\,\mathrm{cm}^{-1}$ to the experimental value**.

The good agreement between experimental and calculated values is rather striking, since in this approximation the electron-electron repulsion is entirely neglected and the calculation is carried out by a method which is not more accurate than simple LCAO MO. Such a result may probably be attributed to the fact that the estimation of the Coulomb and resonance integrals is semi-empirically made so as to involve the effect of electron-electron repulsion implicitly.

As to the dipole moment, on the other hand, the agreement between experimental and calculated values is not good. This discrepancy is probably caused by two main factors. The first is the fact that the electron transfer from the occupied orbital of the iodine molecule to the vacant orbitals of the benzene is neglected in the calculation. The second is the ambiguity engendered in the process of determining the magnitude of many integrals in such a semi-empirical treatment. As is well known, the parameters used for the discussion of chemical reactivity in the simple LCAO MO treatment are often found not suitable for estimating the value of dipole moment, and in this case the reason of this discrepancy may perhaps be that parameters determined semi-empirically are not appropriate for the calculation of dipole moment.

Polycondensed Aromatic Hydrocarbon-Iodine Complexes.—Many experimental studies for polycondensed aromatic hydrocarbon-iodine complexes have been performed. The electric conductivity of these complexes was measured especially, and it was found that a remarkable increase in conductivity was caused by the molecular complex formation. In this paper we calculate the delocalization energy, making use of Eq. 5, in order to get a clue to elucidate the physical properties of these complexes. The delocalization energies obtained are listed in Table II, together with the equilibrium constant[11] of the complex formation and the energy of the highest occupied orbital of aromatic hydrocarbons. The parallelism between the magnitude of the theoretical index and the equilibrium constant is not complete. This discrepancy is owing to many factors pointed out in the previous paper. The most important factor among these seems to be the dispersion force. To estimate roughly the magnitude of the dispersion force, we calculate the potential due to the dispersion force for the benzene-iodine complex by making use of London's formula. London's formula is represented as:

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[9] R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 767 (1953).

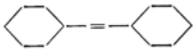
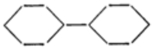
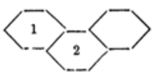
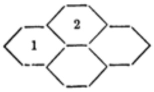
[10] S. Nagakura and J. Tanaka, ibid., **22**, 563 (1954).

* The value of the carbon-iodine distance is estimated by considering the results of X-ray analysis of the bromine-benzene complex[3].

** N. S. Bayliss, *J. Chem. Phys.*, **18**, 292 (1950).

[11] R. Bhattacharya and S. Basu, *Trans. Faraday Soc.*, **54**, 1286 (1958).

TABLE II. THE VALUES OF THE THEORETICAL INDEX AND THE EQUILIBRIUM CONSTANT FOR THE COMPLEX FORMATION BETWEEN AROMATIC HYDROCARBON AND IODINE

Aromatic compound	Ring number*	K[11)]	Delocalization energy**	Energy of the highest occupied orbital
		0.34	1.615	0.504
		0.37	1.579	0.705
		0.62	1.511	0.618
	1	1.06	1.547	0.605
	2	1.06	1.479	0.605
	1	36.49	1.517	0.445
	2	36.49	1.547	0.445
	1	52.35	1.505	0.414
	2	52.35	1.457	0.414

* Ring number indicates the ring that is assumed to associate with the iodine molecule in axial model.

** The value of localization energy listed in Table II is the coefficient of the second order perturbation term in Eq. 5.

$$E_{\mathrm{disp}}=-\frac{3}{2R^6}\frac{I_1\cdot I_2}{I_1+I_2}\alpha_1{}^0\alpha_2{}^0 \tag{9}$$

in which I and α^0 are the ionization potential and the static polarizability respectively, and the suffixes 1 and 2 denote the molecules 1 and 2 respectively, and R is the distance between the two molecules. For the benzene-iodine complex, the values of the ionization potential, static polarizability and distance used in calculation are listed in Table III. The dispersion energy is discovered to be 1.48 kcal.

TABLE III. THE IONIZATION POTENTIAL AND STATIC POLARIZABILITY AND ATOMIC DISTANCE FOR BENZENE AND IODINE MOLECULE AND THEIR COMPLEX

	Benzene	Iodine molecule
Ionization potential, eV.	9.24	9.41
Static polarizability*, cm^3	107×10^{-25}	105×10^{-25}
Distance between benzene and iodine molecule, Å	4.8	

* The static polarizability of iodine molecule is estimated from the value of atomic refraction of iodine atom.

Taking the magnitude of the dispersion force of the benzene-iodine complex into account, we may attain to the following conclusion. It is probably not only the delocalization energy but also the dispersion force and other factors that decides the case of complex formation for the iodine-aromatic hydrocarbon complexes. A detailed discussion of this point will be made in the future.

The Relation between the Delocalization Method and Mulliken's Theory

In both the previous and the present papers, we have proposed the delocalization method and applied this method to the problem of aromatic compound-silver and aromatic hydrocarbon-iodine complexes. The formulas of delocalization energy obtained for both complexes were coincident with Mulliken's theory in its symmetry character, as was earlier pointed out.

In Mulliken's theory the magnitude of charge transfer force was not given in an explicit form, and the symmetry consideration characteristic of his theory is substantially limited to the compound which has some symmetry.

Mulliken's theory was developed by Brown in order to apply to electrophilic aromatic substitutions[12)]. The mathematical interrelation between the chemical reactivity indexes of the frontier theory and Brown's theory was pointed out by some of the present authors[13)]. An analogous relation may be expected between the delocalization method and Mulliken's

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[12)] R. D. Brown, *J. Chem. Soc.*, **1959**, 2224, 2232.

[13)] K. Fukui, K. Morokuma, T. Yonezawa and C. Nagata, *J. Chem. Phys.*, **32**, 1743 (1960).

theory in the case of molecular complex formation if Mulliken's theory is developed in a manner similar to Brown's. This point will be discussed later.

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