

Charge-Transfer Forces in Molecular Compounds. II*

—Benzene-Iodine Complex—

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It is of much interest to inquire whether the structure of the benzene-iodine complex belongs to the symmetry of C_{2v} or C_{6v} . Here the former is called the R (resting) model and the latter the A (axial) model. Some recent experiments on the infra-red spectra of this complex and the observation of the crystalline state of the benzene-bromine complex support the A model of C_{6v} symmetry. In this article the author concludes from a theoretical consideration that the A model is most probable for the structure of the benzene-iodine complex. In the A model, the charge-transfer takes place from ϕ_0 , the MO (molecular orbital) of benzene to $\phi(\sigma_w, 5p)$, the MO of iodine. The energy loss of the charge-transfer state which is involved in adopting the A model instead of the R model, is supplied by the "discreening effect" and the interaction energy between the no-bond state and the charge-transfer state. This interaction energy is far larger in the A model than in the R model.

The stabilization energy, the dipole moment, the charge-transfer spectrum and the oscillator strength are calculated, and we have obtained fairly good agreement with the observations.

§ 1. Introduction

Many interesting observations about the benzene-iodine complex have been reported. This complex shows an intense characteristic absorption near $\lambda=2900 \text{ \AA}$ ¹⁾ which does not appear in case benzene and iodine exist independently. Mulliken²⁾ has explained this absorption theoretically as the charge-transfer spectrum, and estimated the oscillator strength of this spectrum at 0.30 from the experimental value obtained by Green and Ress³⁾. This complex has the dipole moment $0.72D$ ^{2,4)}, which is an evidence of the existence of the charge-transfer state. The stabilization energy has been measured by Bower⁵⁾ as 1.72 kcal/mol.

To a certain extent Mulliken has succeeded in a semi-empirical explanation of the above mentioned observations in view of the charge-transfer mechanism, by means of the R model (Fig. 1). However, Ferguson⁶⁾ has recently concluded from the observation of infra-red spectra of this complex that the A model having the C_{6v} symmetry (Fig. 2) is suitable to this complex. Hassel⁷⁾ has observed that the benzene-bromine complex has the axial structure in the crystalline state, in which the distance between the carbon and the next bromine atom is 3.70 Å. We are

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now much interested in a theoretical explanation of the benzene-iodine complex having the C_{6v} symmetry.

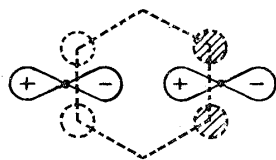


Fig. 1

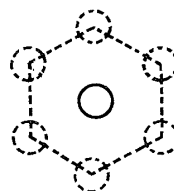


Fig. 2

The solid line represents the MO of iodine, $\phi(\sigma_w, 5p)$. The dotted line represents the MO's of benzene, ϕ_{-1} in Fig.1 and ϕ_0 in Fig. 2.

The reasons why Mulliken has given up the A model and adopted the R model are summarized as follows.

The vacant MO of iodine to which an electron of benzene may transfer is

$$\phi(\sigma_w, 5p) = \{2(1 - S_A)\}^{-1/2}(\chi_A - \chi_{A'}), \quad (1)$$

which is a strongly antibonding MO, spreading along the direction of bond. Here χ_A and $\chi_{A'}$ are $5p$ atomic orbitals of iodine, and S_A is the overlap integral

$$S_A = \int \chi_A \chi_{A'} d\tau. \quad (2)$$

The occupied orbitals of benzene are written as

$$\phi_0 = 6^{-1/2}(\chi_I + \chi_{II} + \chi_{III} + \chi_{IV} + \chi_V + \chi_{VI}) \quad (3)$$

$$\phi_{+1} = 12^{-1/2}(2\chi_I + \chi_{II} - \chi_{III} - 2\chi_{IV} - \chi_V + \chi_{VI}) \quad (4)$$

$$\phi_{-1} = 4^{-1/2}(\chi_{II} + \chi_{III} - \chi_V - \chi_{VI}) \quad (5)$$

where $\chi_I \sim \chi_{VI}$ are $2p\pi$ atomic orbitals of corresponding carbon atoms. In the case of the R model, the charge-transfer takes place from (5) to (1), which is easily verified from symmetry consideration. On the other hand, if we adopt the A model, we cannot but consider the charge-transfer from (3) to (1). This process is energetically more difficult to arise at first glance, because ϕ_0 is lower in energy than ϕ_{-1} .

Next, in the calculation of the energy of the charge-transfer state, the electrostatic attraction between the charged molecules must be taken into account. The mean separation distance between the charged centers of the benzene cation and the iodine anion is greater in the A model than in the R model, and therefore the stabilization in the energy of the charge-transfer state arising from the electrostatic attraction favours the R model. In order to explain theoretically that the A model is suitable to this complex, we must overcome the above mentioned points.

§ 2. Theory with numerical calculation

The ground state wave function of this complex BA (B and A refer to benzene

and iodine respectively) is written as

$$\Psi_N = a\Psi_0 + b\Psi_1, \quad (6)$$

where Ψ_0 is no-bond wave function

$$\Psi_0 = \Psi(BA) = \mathfrak{A} \Psi_B \Psi_A, \quad (7)$$

and \mathfrak{A} is the antisymmetrizer. Further

$$\Psi_B \Psi_A = \phi_B \alpha(1) \phi_B \beta(2) [B][A], \quad (8)$$

in which $[B]$ and $[A]$ denote the configuration of electrons in the occupied MO's of B except ϕ_B , and that of electrons in the occupied MO's of A , respectively. In (8)

$$\phi_B = \phi_{-1} \quad \text{for the } R \text{ model,}$$

$$\phi_B = \phi_0 \quad \text{for the } A \text{ model.}$$

Ψ_1 is the wave function describing the charge-transfer state

$$\Psi_1 = \Psi(B^+ A^-), \quad (9)$$

which is written in detail as

$$\Psi_1 = (2 + 2S_{BA}^2)^{-1/2} (\Psi_I + \Psi_{II}), \quad (10)$$

$$\Psi_I = \mathfrak{A} \phi_B \alpha(1) \phi_A \beta(2) [B][A] \quad (11)$$

$$\Psi_{II} = \mathfrak{A} \phi_A \alpha(1) \phi_B \beta(2) [B][A],$$

$$S_{BA} = \int \phi_B \phi_A dv. \quad (12)$$

The coefficients of (6) have the relation

$$a^2 + 2abS + b^2 = 1, \quad (13)$$

$$S = \int \Psi_0 \Psi_1 dv = \{2/(1 + S_{BA}^2)\}^{-1/2} S_{BA}. \quad (14)$$

As $[B]$ and $[A]$ are regarded as fixed in the calculation, the effect of these electrons may be treated as a part of the effective Hamiltonian. In (6) the mixing of Ψ_1 into Ψ_0 seems to be very small ($a \gg b$), so the second order perturbation theory is an adequate approximation in this case. The ground state energy of this complex is

$$W_N \simeq W_0 - \frac{(H_{01} - SW_0)^2}{W_1 - W_0} \simeq W_0 - \frac{H_{01}^2}{W_1 - W_0}, \quad (15)$$

where

$$W_0 = \int \Psi_0 H \Psi_0 dv, \quad W_1 = \int \Psi_1 H \Psi_1 dv, \quad H_{01} = \int \Psi_0 H \Psi_1 dv. \quad (16)$$

The stabilization energy is

$$\Delta W = H_{01}^2 / (W_1 - W_0). \quad (17)$$

It must be determined from the estimation of the stabilization energy whether the *R* model or the *A* model should be suitable to the benzene-iodine complex. In estimating (17) the denominator ($W_1 - W_0$) takes a smaller value in the *R* model than in the *A* model as mentioned in § 1. Here we are led to use the following approximation for H_{01}' , otherwise it must be treated as a semi-empirical parameter.

$$H_{01}' = \beta S / S_{\beta}, \quad (18)$$

where S_{β} is the overlap integral between $2p\pi$ orbitals of adjacent carbon atoms in benzene, and β is the resonance integral of the corresponding orbitals, of the magnitude -40 kcal/mol.

$$S_{\beta} = \int \chi_I \chi_{II} dv = 0.26.$$

The width of the benzene ring 2.41 Å is nearly equal to the interatomic distance of the iodine molecule 2.66 Å. Therefore, in the *R* model, the $2p\pi$ carbon atomic orbital is almost orthogonal to the $5p$ iodine atomic orbital, and the overlap integral between them becomes nearly zero.

In the case of the *A* model, we may easily understand from the orientations of atomic orbitals that the value of S_{BA} becomes largest. Here we ought to use (3) as ϕ_B and the polarized form of (1) for ϕ_A , which is written as

$$\phi_A = N^{-1/2} (\chi_A - \lambda \chi_{A'}). \quad (19)$$

In order to estimate the parameter λ , we may adopt the following consideration as a reasonable one. The positive charge of benzene in the charge-transfer state is assumed to be at the center of the benzene ring, and the negative charge density about *A* or *A'* atom of iodine is thought to be inversely proportional to the distance between the positive charge of benzene and the *A* or the *A'* atom of iodine respectively. Then we obtain $\lambda = 0.82$.

Thus the overlap integral S is calculated at

$$\left. \begin{aligned} S &= 0.0058 && \text{for the } R \text{ model,} \\ S &= 0.11 && \text{for the } A \text{ model,} \end{aligned} \right\} \quad (20)$$

where the Slater orbitals are used for the carbon and the iodine atomic orbitals and the Mulligan approximation⁸⁾ is used for the heteropolar integral. (20) suggest very small interaction energy for the *R* model, therefore we may conclude that the *R* model is not adequate to this complex. In the following our discussion shall be directed to the *A* model and let us examine how to overcome what Mulliken has pointed out.

The interaction energy H_{01}' is estimated by substituting (18) with (20), and we obtain

$$H_{01}' = -0.72 \text{ eV.} \quad (21)$$

The energy of the no-bond state is

$$\begin{aligned}
W_0 &= \int \Psi_0 H \Psi_0 d\nu \\
&= \int \phi_B \alpha(1) \phi_B \beta(2) (H_B + H_A) \phi_B \alpha(1) \phi_B \beta(2) d\nu \\
&\simeq 2 \int \phi_B H_B \phi_B d\nu \\
&\cong -2I_B \\
&\cong -2(9.2 + 1.7) \text{ eV}.
\end{aligned} \tag{22}$$

Here the electronic Hamiltonian is the sum of the self-consistent one-electron Hamiltonian and they are considered to be constructed by two parts, part *B* and part *A*. I_B is the second ionization potential of benzene and is estimated to be the sum of the first ionization potential 9.2 eV and $-\beta = 1.7$ eV.

On the other hand, the charge-transfer state, as has been written in (11), has the positive hole in part *B*. In the evaluation of the energy of this state we must take account of the effect of this positive hole in the electronic Hamiltonian, that is to say, the Hamiltonian referred to *B* is to be H_B^+ , then

$$\begin{aligned}
W_1 &= \int \Psi_1 H \Psi_1 d\nu \\
&= \int \phi_B \alpha(1) \phi_A \beta(2) (H_B^+ + H_A) \phi_B \alpha(1) \phi_A \beta(2) d\nu \\
&\cong \int \phi_B H_B^+ \phi_B d\nu + \int \phi_A H_B^+ \phi_A d\nu + \int \phi_A H_A \phi_A d\nu,
\end{aligned} \tag{23}$$

where

$$\int \phi_A H_A \phi_A d\nu \cong -E_A \cong -1.8 \text{ eV} \tag{24}$$

in which E_A is the electron affinity of the iodine molecule and has been reported at the magnitude of larger than 1.8 eV⁹⁾

$$\int \phi_A H_B^+ \phi_A d\nu \cong -1/r_e = -3.3 \text{ eV} \tag{25}$$

seems to be a good approximation as the inter-molecular distance is very large, where r_e is the distance between the positive charge of benzene and the mean charge distribution of the iodine molecule. Next,

$$\begin{aligned}
\int \phi_B H_B^+ \phi_B d\nu &= \int \phi_B H_B \phi_B d\nu + \Delta \\
&= -I_B + \Delta.
\end{aligned} \tag{26}$$

Here Δ is the effect arisen from that the Hamiltonian has changed from H to H^+ , and called the "discreening effect" hereafter. It is estimated approximately as the difference of the Coulomb interactions between above two states,

$$\Delta \simeq (\delta - \delta^+) / r_i. \quad (27)$$

Here r_i is the mean distance between the $2p\pi$ electron and the positive charge at the center of the benzene ring, and δ and δ^+ are the orbital exponents of the neutral $2p\pi$ carbon atom and that of the positive carbon ion respectively. r_i is easily estimated at 1.65 Å (3.12 a.u.), then

$$\begin{aligned} \Delta &\simeq (1.625 - 1.80) / 3.12 \\ &= -0.056 \text{ a.u.} = -1.52 \text{ eV.} \end{aligned}$$

In (26), Δ is in appearance the stabilization energy for the electron left in ϕ_B , but the above estimation of Δ in (27) contains all stabilization energies for the electrons not only in ϕ_0 but also in ϕ_{+1} and ϕ_{-1} of benzene. And this treatment is fortunately valid in this problem.*

From the foregoing results we obtain

$$\begin{aligned} W_1 - W_0 &= I_B - E_A - 1/r_e + \Delta \\ &= 4.3 \text{ eV.} \end{aligned} \quad (28)$$

Now we calculate the stabilization energy, using (28) and (21) combined with (17),

$$\Delta W = 0.12 \text{ eV} = 2.8 \text{ kcal/mol.}$$

The coefficients a and b in (6) are evaluated by using

$$b/a = -H_{01}' / (W_1 - W_0) \quad (29)$$

and the normalization condition (13), at

$$a = 0.97, \quad b = 0.16. \quad (30)$$

The dipole moment of the ground state

$$\mu_N = -e \int \Psi_N \sum r_i \Psi_N dv \quad (31)$$

is calculated in quite the same way as Mulliken²⁾ has used, at

$$\mu_N = 0.94 \text{ D.}$$

In order to calculate the charge-transfer spectrum and the oscillator strength associated with it, the excited state shall be considered.

$$\Psi_E = a^* \Psi_1 - b^* \Psi_0, \quad (32)$$

$$a^{*2} - 2a^*b^*S + b^{*2} = 1. \quad (33)$$

The energy of the excited state is given as

* For this discussion the author is very much obliged to Prof. S. Nagakura.

$$W_E \cong W_1 + \frac{(H_{01} - SW_1)^2}{W_1 - W_0} \cong W_1 + \frac{H_{01}^2}{W_1 - W_0}. \quad (34)$$

The frequency of the charge-transfer spectrum is given as

$$h\nu = W_E - W_N = W_1 - W_0 + 2H_{01}^2 / (W_1 - W_0) \quad (35)$$

and we obtain

$$\nu = 36,500 \text{ cm}^{-1}.$$

The coefficients a^* and b^* are estimated at

$$a^* = 1.00, \quad b^* = 0.27. \quad (36)$$

The oscillator strength

$$f = (4.704 \times 10^{-7}) \nu \mu_{EN}^2,$$

where μ_{EN} is the transition dipole, is calculated by the similar procedure to that of calculating the ground state dipole moment, and then we obtain

$$f = 0.34.$$

§ 3. Discussion and conclusion

The calculated results are tabulated in Table 1, where we can see fairly good agreement between the calculated results and the observed values. The charge-transfer spectrum $36,500\text{cm}^{-1}$ in the observed values of Table 1 is the value which is obtained by adding $2,000\text{cm}^{-1}$ to the actual observed value as a solvent effect³⁾.

Table 1.

	calc.	obs.
stabilization energy (kcal/mol)	2.8	1.72 ⁵⁾
dipole moment (Debye unit)	0.94	0.72 ²⁾
charge-transfer spectrum (cm^{-1})	36,500	36,500 ¹⁾
oscillator strength	0.34	0.30 ²⁾

From the preceding calculations we can conclude as follows: The geometrical structure of the benzene-iodine complex is not the *R* model having the symmetry of C_{2v} , which has been postulated by Mulliken, but the *A* model having the symmetry of C_{6v} , which is supported by the recent experiments. We have concluded that the *R* model is not suitable to this complex by the estimation of the interaction energy between the no-bond state and the charge-transfer state of this complex. Mulliken has not exactly calculated the overlap integral between these two states, but has simply assumed for it the value of 0.1, which is, however, obtained when we adopt the *A* model. The estimation of the overlap integral is essentially im-

portant, so long as it is assumed that the interaction energy is proportional to the value of the overlap integral, as has been done in (18). Though the Slater orbital of high quantum number, say the $5p$ atomic orbital of iodine, does not seem to be adopted as a fully accurate one, the semi-qualitative treatment may be possible under the approximations assumed in this article. Also we may note that Mulliken has used 1.2 eV for the electron affinity of the iodine molecule (the observed value is larger than 1.8 eV.)

The charge-transfer does not always take place from the highest occupied orbital of the charge-donating molecule to the lowest vacant orbital of the charge-accepting molecule. In other words, we should not expect the simple relation between the first ionization potentials of the charge-donating molecules and the charge-transfer spectra of the complexes. In this problem we cannot but consider the charge-transfer from ϕ_0 of benzene to $\phi(\sigma_u, 5p)$ of iodine, where the former is not the highest occupied orbital of benzene. The energy loss caused by adopting the A model is compensated by the introduction of the "discreening effect" which is the stabilization energy for the electrons left in the MO's of the charge-donating molecules. This effect is originated from the change of the orbital exponents of the atomic orbitals of the charge-donating molecule, corresponding to the change from the neutral state to the positively charged state of the molecule.

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