Theoret. chim. Acta (Berl.) 23, 67—74 (1971)

SCFMO Calculation of the 1:1 Charge-Transfer Complex between Benzene and p-Benzoquinone by the Variable Integrals Method II*

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Received February 16, 1971

The charge-transfer complex system between benzene and p-benzoquinone is treated as a single conjugated system of π-electrons and its π electron states are calculated by the Variable Integrals Method II. For three models of the charge-transfer complex, potential energy curves, stabilization energies, orbital energy diagrams, electron densities, bond orders, dipole moment and electronic transition energies are discussed. The agreement between theory and experiment is satisfactory as for as the electronic spectra are concerned.

Der Ladungsübertragungs-Komplex zwischen Benzol und *p*-Benzochinon wird als ein einziges konjugiertes π-Elektronensystem behandelt. Seine π-Elektronenzustände werden nach der „Methode II der Variablen Integrale" berechnet. Für drei Modelle des Komplexes werden die Potentialkurven, die Stabilisierungsenergien, die Diagramme der Orbitalenergien, die Elektronendichten, die Bindungsordnungen, die Dipolmomente sowie die elektronischen Übergangsenergien untersucht. Die Übereinstimmung mit dem Experiment ist für die Elektronenspektren zufriedenstellend.

Calcul des états électroniques π par la méthode des intégrales variables II pour le complexe de transfert de charge entre le benzène et la *p*-benzoquinone considéré comme un système conjugé unique. Discussion de trois modèles de complexe de transfert de charge: courbes d'énergie potentielle, énergies de stabilisation, diagrammes d'énergie orbitale, densités électroniques, moment dipolaire et énergies de transition électronique. L'accord entre théorie et expérience est satisfaisant tout au moins pour les spectres électroniques.

1. Introduction

In the preceding paper [1] we have proposed a modified Pariser-Parr-Pople method, the Variable Integrals Method II (VI/2). This method needs no guess work in finding a set of suitable parameters to calculate the electronic spectra of a molecule in question. This method has been applied to a large number of different types of molecules with great success [1, 2].

In this paper we would like to apply this method to the 1:1 charge-transfer complex between benzene and *p*-benzoquinone to see the applicability of this method to intermolecular interaction such as charge-transfer complexes.

Not a few papers on charge-transfer (CT) complexes have appeared in the past few years, from both experimental and theoretical points of view. Most of the theoretical papers on CT complexes have used valence bond method [3]. Dewar's molecular orbital approach to CT complexes [4] uses perturbation method. Fukui and coworkers' [5] delocalization approach is a simple LCAO

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* Presented at the 2nd Symposium on Structural Organic Chemistry, Osaka, November, 1969.

method. In this method the atomic orbitals of both the donor and the acceptor are considered explicitly and the stabilization energy of the system is calculated by perturbation method. Recently direct calculations on the whole complex have been attempted [6, 7, 8]. Flurry [6] has presented a simple semiempirical linear combination of molecular orbitals method for CT complexes. Semiempirical SCF-MO-CI method has also been applied to CT complex [18]. Tetracyanobenzene and tetracyanoethylene complexes have been treated with the molecules in molecules method [7, 8].

In the present paper the whole system of the benzene-p-benzoquinone 1:1 complex is directly treated with the semiempirical molecular orbital method as if it is one molecule.

2. Method of Calculation

The method used in this study is the Variable Integrals Method II, (VI/2) all β, proposed and used in the preceding papers [1, 2]. So the details of the method are not given here.

For the sake of simplicity only the π-electrons are taken into consideration in this study. The whole system of the complex is regarded as one molecule. And only the cases where the benzene ring plane is parallel to the *p*-benzoquinone ring plane are considered. In the computation three models, A, B, and C, are considered. These models are illustrated in Fig. 1. The coordinate axis and the numberings of the atomic orbitals are also given in Fig. 1. The model C is just the intermediate configuration between the models A and B. The molecular structural data of benzene and *p*-benzoquinone are taken from Ref. [9]. The bond lengths and bond angles in the complex are assumed to be equal to those of free benzene and free *p*-benzoquinone.

In the computation the gravity of benzene ring *G*' (*X*, *Y*, *Z*) is moved in the three dimensional space changing the *X*- and the *Y*-coordinates with the interval of 1 A and the *Z*-coordinate with the interval of 0.25 A from *Z* = 2.0 A to 3.5 A

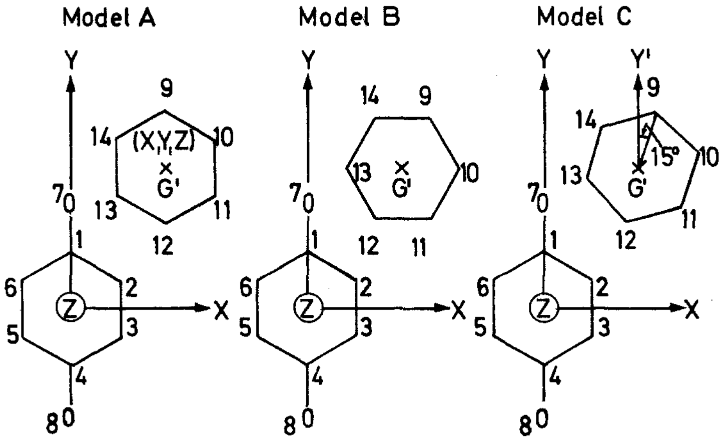

Fig. 1. Computational models for benzene-*p*-benzoquinone 1:1 complex

for the models A and B. The calculations for the model C are only carried out at $X=0$ A and $Y=3$ A changing the Z-coordinate with the interval of 0.25 A from $Z=2.0$ A to 3.5 A.

The stabilization energy of the system for each configuration is calculated as follows:

$$\Delta E(X, Y, Z)=E_B^\pi+E_Q^\pi-E_C^\pi-\sum_{i_B, j_Q} Z_{i_B} Z_{j_Q} e^2/R_{i_B j_Q} \tag{1}$$

where E_B^π, E_Q^π and E_C^π denote the total π-electronic energies of benzene, *p*-benzoquinone and the 1:1 charge-transfer complex, respectively. The last term in the formula (1) is the core-core repulsion energy between the core of benzene and that of *p*-benzoquinone.

3. Results and Discussions

As examples, the potential energy curves of the model A for several sets of the X- and Y-components are shown in Fig. 2. The potential energy curves given by the models A and B are similar to each other. The Z-coordinate which gives the maximum stabilization energy for each set of (X, Y), $Z_{\max}$, and the stabilization energy at the point $(X, Y, Z_{\max})$, $\Delta E_{\max}^{(X,Y)}$, are summarized in Table 1 for the models A and B. The both models give similar $Z_{\max}$- and similar $\Delta E_{\max}^{(X,Y)}$-values to each other, that is, it is presumed that the stabilization energy of the system may be nearly indifferent to the rotation of the benzene ring around its C_6-axis. From Table 1 it is presumed that the system is most stable around the point (0, 3A, 2.5A). The stabilization energy calculated at the point (0, 3A, 2.5A) with the model A is

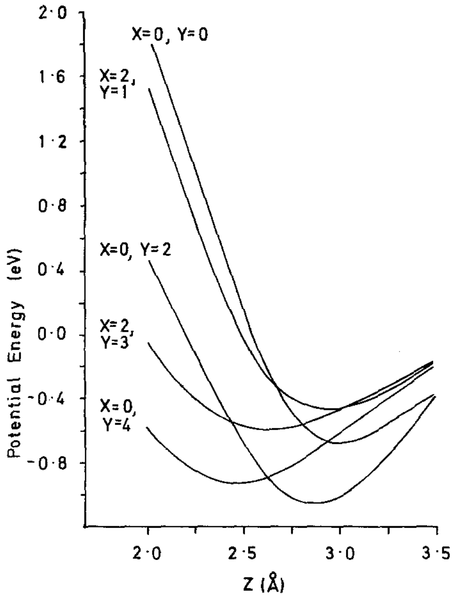

Fig. 2. Potential energy curves of benzene-*p*-benzoquinone 1:1 complex calculated with model A

Table 1. *Stabilization energy of the system,* $\Delta E_{\max}^{(X,Y)}$(eV) *and Z-coordinate,* $Z_{\max}(A)$ *(in parenthesis) at the minimum point of the potential energy curve for each set of* (X, Y) *with Model A and Model B*

	Model A				Model B			
$Y \diagdown X$	0	1	2	3	0	1	2	3A
5A	0.631 (1.25)	0.591 (2.00)	0.538 (1.75)		0.633 (2.25)	0.574 (2.00)	0.525 (1.75)	
4	0.922 (2.50)	0.758 (2.50)	0.571 (2.50)		0.892 (2.50)	0.779 (2.50)	0.599 (2.25)	
3	1.135 (2.50)	0.913 (2.75)	0.579 (2.75)		1.132 (2.75)	0.910 (2.50)	0.565 (2.50)	
2	1.042 (2.75)	0.876 (2.75)	0.501 (2.75)		1.051 (2.75)	0.849 (2.75)	0.527 (2.75)	
1	0.769 (3.00)	0.702 (3.00)	0.457 (3.00)	0.186 (3.00)	0.769 (3.00)	0.724 (3.00)	0.438 (3.00)	0.173 (2.75)
0	0.668 (3.00)	0.706 (3.00)	0.433 (3.00)	0.120 (3.25)	0.690 (3.00)	0.661 (3.00)	0.398 (3.00)	0.120 (3.00)

1.135 eV. The model C shows the potential energy minimum at about $Z=2.5$A if the Z-coordinate is changed at $X=0$A and $Y=3$A and the stabilization energy at (0, 3A, 2.5A) is 1.132 eV. The stabilization energy at (0, 3A, 2.5A) given with the model B is 1.123 eV. Therefore the benzene ring may rotate freely around its C_6-axis near the minimum point of the potential energy surface of the system. The enthalpy of formation of the 1:1 complex is ca. -1.8 kcal/mole according to Kuboyama and Nagakura [10]. Therefore the calculation in this study rather overestimates the stabilization energy. In general the interplanar distances are greater than 3A in molecular crystals such as π–π complexes. For instance the interplanar distance of quinhydrone in the crystal state is 3.19A according to the x-ray chrystallographic analysis by Sakurai [11]. Unfortunately it seems that there have been no x-ray chrystallographic analysis of benzene-*p*-benzoquinone system.

The orbital energy diagram of the system for model A at $X=0$ and $Y=3$A against the Z-coordinate is shown in Fig. 3. The orbital energy diagrams given by the three models are similar to one another. At a long distance the molecular orbitals are well correlated with the molecular orbitals of the free component molecules. The orbital energies of the complex begin to change at about $Z=2.5\sim2.75$A in each model.

The molecular diagrams of the system at (0, 3A, 2.5A) are shown in Fig. 4 with those of free component molecules. The molecular diagrams given by the three methods are similar to one another and also similar to those of the component molecules. This suggests that there may be present no appreciable change in the structures of the component molecules in complex formation. The bond order between the atomic orbitals 1 and 12 is around -0.1 for the models A, B and C at (0, 3.0A, 2.5A).

The change of the dipole moment and the charge transferred from benzene to *p*-benzoquinone at $X=0$ and $Y=3$A are shown against the Z-coordinate

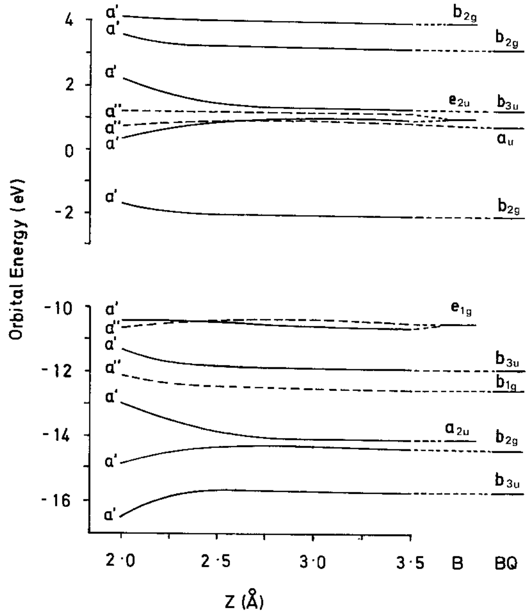

Fig. 3. Orbital energy diagram of benzene (B)-*p*-benzoquinone (BQ) 1:1 complex calculated with model A at $X=0$ and $Y=3$A

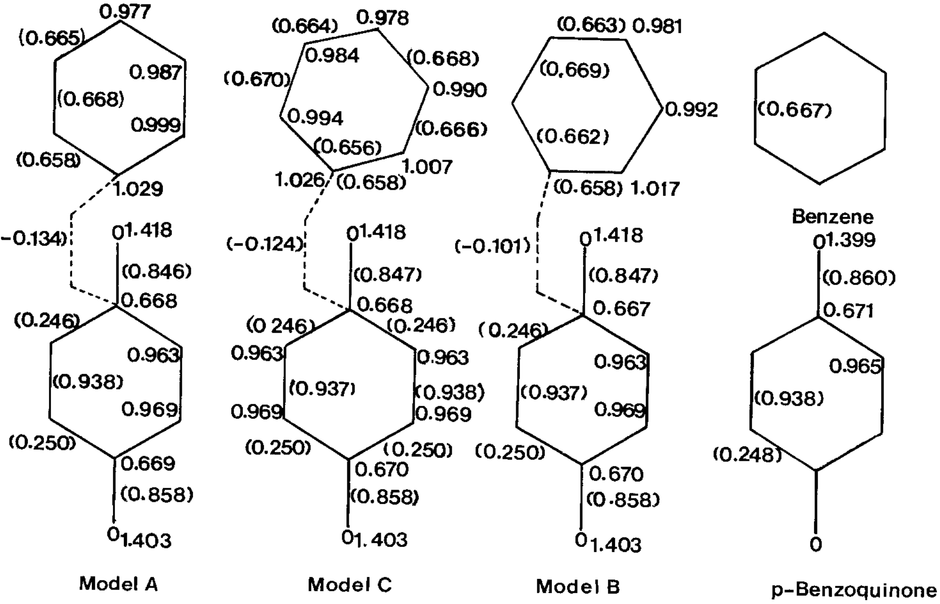

Fig. 4. Electron densities and bond orders (in parentheses) of benzene-*p*-benzoquinone 1:1 complex calculated with model A, B and C at $X=0$, $Y=3$A and $Z=2.5$A and those of benzene and *p*-benzoquinone

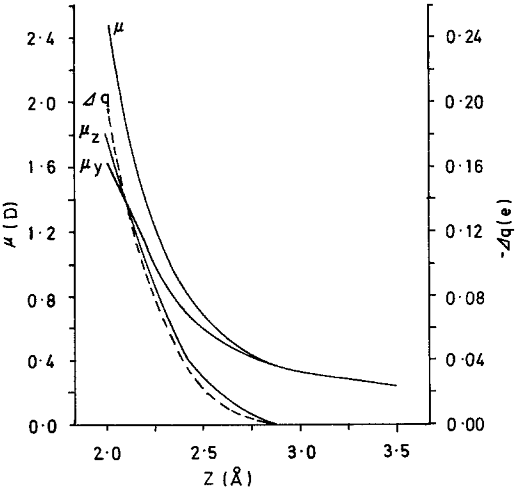

Fig. 5

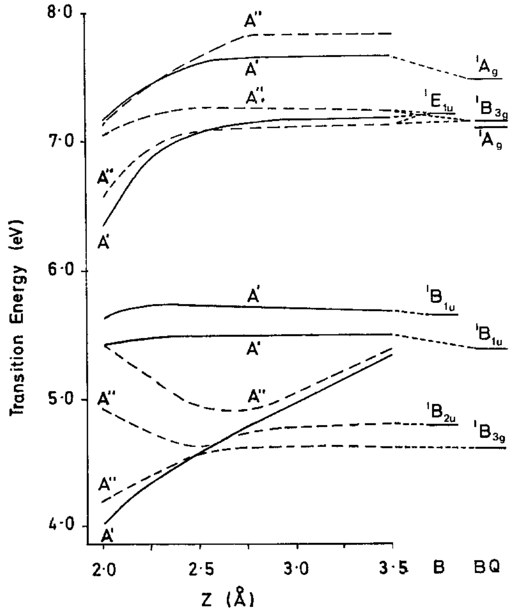

Fig. 6

Fig. 5. Dipole moment, μ, and the amount of charge migrated from benzene to *p*-benzoquinone, Δq, in the ground state of benzene-p-benzoquinone 1:1 complex calculated with model A at $X=0$ and $Y=3$ A

Fig. 6. Transition energy diagram for benzene (B)-*p*-benzoquinone (BQ) 1:1 complex calculated with model A at $X=0$ and $Y=3$ A

in Fig. 5 for the model A. As is shown in Fig. 5, it is presumed that the charge migration begins to increase steeply at about $Z=2.25$ A. The charge migrated from benzene to *p*-benzoquinone at (0, 3.0 A, 2.5 A) is only about $-0.02\,e$, that is, in the ground state the charge is migrated only slightly and the ground state is quite near the free component molecules.

The transition energy diagrams for the model A is shown in Fig. 6. At a long distance the lower energy transitions are well correlated with the component molecules. The two models A and B give quite similar transition energy diagrams. The third and the fourth transitions at $Z=3.5$ A are the intermolecular charge-transfer transitions associated with electron transfer from benzene to *p*-benzoquinone. The energies of these two transitions decrease rapidly as the Z-coordinate decreases. And at about $Z=2.6$ A the two longest wavelength transitions become the intermolecular charge-transfer transitions. This tendency is also observed in the model C.

The transition energies calculated at (0, 3.0 A, 2.5 A) with the models A, B and C and those of the free component molecules are shown in Table 2. From this Table the strong absorption band observed at about 4.35 eV [12] is assigned as the intermolecular charge-transfer band composed of two transitions in accordance with experimental result.

Table 2. *Calculated* $^1\pi$-$^1\pi^*$ *electronic transition energies in* eV. *Benzene-p-benzoquinone* 1:1 *system at* $X = 0$ Å, $Y = 3$ Å *and* $Z = 2.5$ Å

	Model A				Model B			Model C			Obsd.	
	E	f	type		E	f	type	E	f	type	E	f
A″	4.545	0.004	CT	A′	4.527	0.048	CT	4.532	0.038	CT	4.35ᵃ (12)	~0.1 (13)
A′	4.561	0.058	CT	A″	4.576	0.004	LQ + CT	4.572	0.016	CT + LQ		
A″	4.646	0.002	LQ	A″	4.728	0.008	CT + LQ	4.682	0.011	LQ + CT		
A″	4.962	0.003	LB + CT	A′	4.884	0.021	CT + LB	4.929	0.008	LB + CT		
A′	5.479	0.855	LQ	A′	5.483	0.834	LQ	5.481	0.844	LQ		
A′	5.723	0.654	LB	A″	5.718	0.331	CT + LB	5.720	0.663	LB + CT		

CT: contribution from charge-transfer configuration
LB: contribution from localized excitation configuration in benzene
LQ: contribution from localized excitation configuration in p-benzoquinone
ᵃ in CCl_4

	E	f	E_{Obsd}	$\log \varepsilon$	
Benzene					
$^1B_{2u}$	4.808	0.0	4.84ᵃ	2.3	(14)
$^1B_{1u}$	5.645	0.0	6.05		(16)
$^1E_{1u}$	7.223	2.466	7.0		(17)
p-Benzoquinone					
$^1B_{3g}$	4.603	0.0	4.40ᵃ	2.51	(15)
$^1B_{1u}$	5.383	1.006	5.0ᵃ	4.2	
^1A_g	7.119	0.0			

In conclusion the calculated transition energies of the complex at the most stable configuration in this calculation was reasonable. But unfortunately the estimated interplanar distance was rather shorter than the expected and the calculated stabilization energies was too large at the most stable configuration. These defects may have been caused by the neglect of the σ-framework, and by the use of Slater's atomic orbitals. In relation to this it has been pointed out that the intermolecular overlap integrals are markedly underestimated when they are evaluated using Slater's atomic orbitals [7, 19].

Therefore it may be important to try the calculations by taking the σ-electrons explicitly into account and by using more optimized atomic orbitals such as SCF atomic orbitals.

The calculation has been carried out on a FACOM 230–60 computer at the computation center of the Kyoto University.

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