The Visible Absorption Spectra and Binding Energy of Quinhydrone-Type Molecular Compounds

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Introduction

Although quinhydrone and homologous molecular compounds have been well known for many years, the nature of the intermolecular binding force has not yet been thoroughly clarified. Recently, some interesting results concerning this problem have been obtained. Osaki and Matsuda[1] have, through the analysis of the x-ray pattern of quinhydrone crystal, determined the structure of this compound. K. Nakamoto[2] observed the dichroism of the visible absorption spectra of quinhydrone crystal, and found that "the spectrum by the light with the electric vector abundant with the parallel component to the benzene ring is more bathochromic and hyperchromic than the one with the electric vector abundant with the perpendicular component to the benzene ring". Seki and others[3] determined the heat of formation of quinhydrone from its component-molecules as 5.39 kcal./mol. by the measurements of the heat of solution and the vapor pressure. This would be the first reliable experimental data of the binding energy of this compound.

The present author has determined the heat of association of quinhydrone and some homologues in dilute solutions by measuring quantitatively the absorption spectra of the solutions of quinone and the compounds which combine with it (in this research, hydroquinone, dimethylhydroquinone and phenol, hereafter called B compounds) in various concentrations and temperatures. The visible absorption spectra of these systems in various concentrations were measured by L. Michaelis and S. Granick. They treated the results with the theory of chemical equilibrium and reported that the molecular compounds in solutions are in a dimeric form, $Q_1 \cdot B_1$, without regard to their compositions in the solid state. However, they had no intention of deriving the heat of association from these measurements, though the determination of these values is, in principle, possible.

In the second part of this paper, a structure of these molecular compounds will be proposed on the basis of some experimental knowledge concerning these compounds. On this assumed structure, the origin of the binding force and the visible absorption spectra of these molecular compounds are discussed.

Part I. The Determination of the Heat of Association in Solution by the Measurements of the Visible Absorption Spectra

Principle of the Experiment

The principle of deriving the experimental equilibrium constant of association and the molecular extinction coefficient of the molecular compound is the same as that which was employed by Benesi and Hildebrand.[5] Namely, if we designate the total molar concentration of quinone and a B compound by c^0_Q and c^0_B, the extinction coefficient of the molecular compound by d_X, and its molecular extinction coefficient by ε_X, then the linearity relation

$$c^0_Q/d_X = 1/(K \cdot \varepsilon_X \cdot c^0_B) + 1/\varepsilon_X \qquad (1)$$

(1) Osaki and Matsuda, *Acta Cryst.* (to be published). Their results were quoted in Nakamoto's paper (ref. (2)).

(2) K. Nakamoto, *J. Am. Chem. Soc.* **74**, 1738 (1952).

(3) S. Seki, *Kagaku*, **22**, 416 (1952). Detailed information will be published in the near future in this bulletin.

(4) H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2703 (1949).

holds between (c^0_Q/d_X) and $(1/c^0_B)$, if the equilibrium is expressed by the formula $Q+B \rightleftarrows QB$ and if $c^0_Q \ll c^0_B$. We found that equation (1) really holds for all molecular compounds we investigated, agreeing with Michaelis' results. Then, we can calculate the equilibrium constant K and the molecular extinction coefficient ε_X using the least square method.

Since quinone, unfortunately, has absorption in the visible region, it is necessary to select some wave lengths which are most suitable for the experiment, i. e., wave lengths, in which the absorption of the molecular compound is sufficiently strong and the absorption of quinone is negligibly small. In the case in which the absorption of quinone is not small enough to be ignored even in the most suitable region of wave length, d_X was calculated by the formula

$$d_X = d_{obs} - d'_Q - d^0_B \qquad (2)$$

where d^0_Q and d'_B are the absorption of the total quinone and the B compound present in the solution including those which are associated. These d^0_Q and d^0_B were calculated from the molecular extinction coefficients of these compounds in a free state and their concentrations in each ternary system.* Of course, we should use d_Q and d_B that are the absorption of free quinone and the B compound present in the system instead of the d^0_Q and d^0_B. However, the small magnitude of d^0_Q and d^0_B as compared to d_X and the small degree of association of the molecular compounds reasonably permit the approximation.

The heat of association ΔH can be determined from the equilibrium constants at two different temperatures by use of the following formula

$$\Delta H = -RT_1 \cdot T_2/(T_1-T_2) \cdot \ln K_1/K_2 \qquad (3)$$

Experimental

Spectrophotometric measurements were made with the Beckman spectrophotometer, Model DU.

The solvent used should have the following properties:

1. Its absorption in the visible region is negligible.
2. It dissolves considerable amounts of the compounds under the investigation.
3. It has no particular influence on the association of the molecular compounds.

Cyclohexane was used as a solvent which generally fulfills these conditions. However, only for the case of quinone-hydroquinone system, 0.05M. aqueous solution of hydrogen chloride was used, since hydroquinone is quite insoluble in cyclohexane. It is known that hydroquinone dissolved in water is a little unstable under the contact of air. However, we can believe that this compound remained unchanged in such a dilute acid as above mentioned during the spectrophotometric measurements, because it was verified that the ultraviolet absorption spectrum of this compound in such a solution did not change at all for at least 30 hours.

The method of purification of cyclohexane and phenol was described elsewhere.[6] Quinone was synthetized by the oxydation of hydroquinone by sodiumbichromate,[7] and recrystalized several times out of benzene (m. p. 114—115°C). Hydroquinone was recrystalized from mixtures of benzene and methanol (m. p. 172—173°C). Dimethylhydroquinone was recrystalized from methanol (m. p. 56.0—56.2°C). The ultraviolet absorption spectra of all these compounds were checked before experiment and identity of them with the results described in literatures was confirmed.

During the measurement of absorption, the constancy of the temperature of the samples was maintained by use of a thermospacer equipped in the spectrophotometer (±1°C). Stoppered cells, which were 1 cm in width, were used.

Results

The approximate ranges of the concentrations of quinone and the B compounds in each spectrophotometric measurements were given in Table 1. These ranges of concentration were chosen so that the extinction coefficients of the ternary systems at the optimum wave lengths lie between 1 and 2. In order to apply Eq. (1), the concentration of the quinone were always made below 10% of that of the B compounds. This also decreases the error due to the visible absorption of quinone.

Table 1

	concn. of quinone	concn. of B
1	0.0033 M	0.05—0.46 M
2	0.0045 M	0.06—0.4 M
3	0.003 M—0.007 M	0.15—1.2 M

1: quinone-hydroquinone system
2: quinone-phenol system
3: quinone-dimethylhydroquinone system

For the purpose of testing the accuracy of the values derived, the same experiments were made for more than two wave lengths. The results were shown in Table 2. Since in the cases of the quinone-phenol and quinone-dimethylhydroquinone systems the attempt to derive ε_X's for the higher temperatures was unsuccessful, ε_X's for the lower temperatures were used in the calculation of K's for the higher temperatures, by the assumption that there is no great difference between ε_X's foe these two temperatures respectively. Although the values given in this table

* In this calculation, it was assumed that the absorption spectra of quinone and the B compounds are not shifted from those in a free state. This assumption is necessary, bnt, strictly speaking, is not in general true. For example, hydrogen-bonding between quinone and a B compound may cause a slight shift of their spectra.

(5) H. Tsubomura, *J. Chem. Soc. Japan*, **73**, 920 (1952).
(6) Organic Syntheses, **1**, 469.

Table 2

The ε_1, K_1 and the ε_2, K_2 correspond to the data for lower and higher temperatures respectively

B compound	wave length (in mμ)	ε_1	ε_2	K_1	K_2	K_1/K_2	ΔH (kcal./mol.)
hydroquinone	500	630	730	1.01	0.49	2.1	4.8
	520	510	600	1.10	0.46	2.4	5.7
phenol	330	1180	1180	1.23	0.71	1.7	4.4
	350	1110	1110	1.11	0.57	1.9	5.0
	400	850	850	1.06	0.56	1.9	5.0
dimethyl-hydroquinone	380	340	340	0.51	0.30	1.7	4.2
	390	310	310	0.69	0.43	1.6	3.8
	400	355	355	0.61	0.43	1.4	2.7

Table 3

B compound	solvent	K_1 (t°C)	K_2 (t°C)	K_1/K_2	ΔH (kcal./mol.)	λ_{max} (mμ)	ε_{max}
hydroquinone	0.05 M HCl aq. solution	1.06 (20°)	0.48 (49°)	2.2	5.2	440	890
phenol	cyclohexane	1.13 (16°)	0.61 (39°)	1.9	4.8	315	1200
dimethyl-hydroquinone	cyclohexane	0.60 (25°)	0.39 (49°)	1.6	3.5	413	370

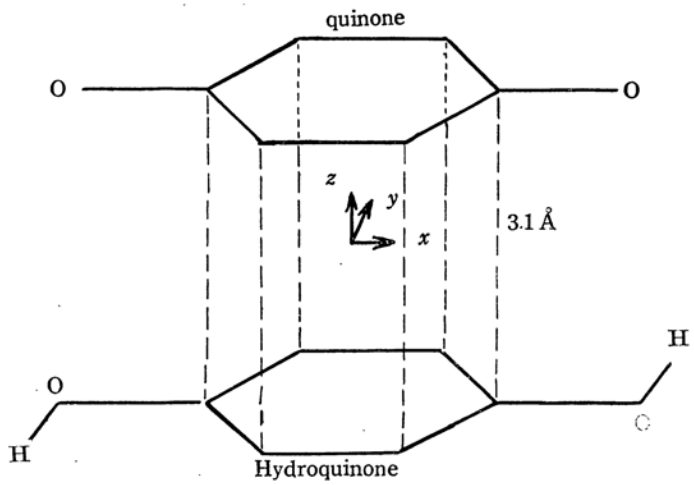

Fig. 1.

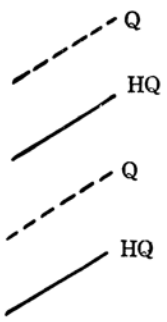

Fig. 2

are not perfectly accurate, it may be regarded that they show us the general trends of the binding energies and the absolute intensities of the visible absorption of these molecular compounds. The average values of K_1, K_2, K_1/K_2 and ΔH, with λ_{max} and ε_{max} which were obtained from the measurements of the whole spectra were given in Table 3.**

Detailed discussion on these results will be given in the second part of this paper with the theoretical treatment of these molecular compounds.

** It is to be noted here that we should be careful in comparing the heat of association of quinone-hydroquinone system with that of quinone-phenol system because these two were measured in different solvents.

Part II. Theory of the Intermolecular Binding Energies and the Electronic States of Quinhydrone and Homologous Molecular Compounds

The molecular structure of quinhydrone and homologues

As previously mentioned, quinhydrone and homologous molecular compounds in dilute solutions are of the form $Q_1 \cdot B_1$. We assume the structures of these associated molecules as those in which two benzene rings are piled up so that one ring is situated just above the other and the planes of these two rings are parallel. For example, the structure of quinhydrone is assumed as given in Fig. 1.

The basis of this assumption is as follows: The

occurance of a new visible absorption in these molecular compounds shows that there is considerable electronic interaction between molecules. Therefore, the structure of the molecular compound must be assumed in such a way as to make an electronic interaction between molecules possible. The structure shown in Fig. 1 will correspond to the strongest electronic interaction and smallest steric repulsion between two component-molecules. On the other hand, the X-ray analysis of Osaki and Matsuda shows that, in the quinhydrone crystal, the quinone and hydroquinone molecules are piled up one upon another in a way shown in Fig. 2; this structure differs from the one shown in Fig. 1 in that the benzene ring of, e. g., quinone is not situated just above the benzene ring of, e. g., hydroquinone. It may be conceived that this deformation is caused by the complicated interacting forces between every atom in the crystal. However, in a dilute solution, where the quinhydrone molecules are separated from each other, there is no reason for the centers of the two benzene rings not to lie on a common normal.

Here, a note on the binding state of the hydrogen atom in quinhydrone should be given. M. Davies[8] measured the infrared absorption spectra of quinhydrone crystal in the 3 μ region and found a peak at 3.10 μ corresponding to the hydroxyl stretching mode. Applying Badger's rule, he was lead to the conclusion that the hydroxyl bond distance is about 1.0Å, which is nearly the same as that of alcohol. According to his results, it is reaonably accepted that the two hydrogen atoms in quinhydrone are definitely bonded to the oxygen atoms, and it is improbable that a peculiar valency state exists in which the hydrogen atoms are equally bonded to the two molecules. In other words, quinhydrone is made up of quinone and hydroquinone molecules which are mutually perturbed.

The nature of the binding energies of quinone and the B compounds

It can be definitely concluded that hydrogen bonding is not a substantial cause of the binding of quinone and the B compounds, from the fact that some compounds which have no group acting as a proton donor, e. g., dimethylhydroquinone, can also combine with quinone.

If we assume the structures of the molecular compounds to be as shown in Fig. 1, it will be clear that a hydrogen bond is unable to form between two component-molecules. For the hydroxyl group in a normal hydroquinone or phenol lies in the plane of benzene ring and, therefore, is nearly perpendicular to the line connecting the two oxygen atoms of quinone and hydroquinone or phenol. It is evident that in such a structure a hydrogen bond cannot be formed, since this bond is believed to be mainly electrostatic. If the hydrogen atom of hydroquinone elevates itself from the plane of the ring, hydrogen bond would be formed. However, in this case the conjugation of the lone pair electron of oxygen with the benzene π-electrons which give rise to a considerable stabilization of the hydroquinone molecule would be destroyed. Of course, it is supposed that there are hydrogen-bonded quinone and hydroquinone or phenol molecules in a dissolved state. However, the hydrogen bond will probably be formed between molecule-pairs which, different from those of which molecular compound is composed, are situated in such a manner as shown in Fig. 3. We can suppose that the electronic interaction

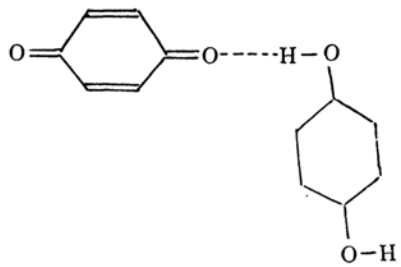

Fig. 3.

between these hydrogen-bonded molecules is negligibly small, and therefore the visible absorption spectra cannot arise from them. As the heat of association given in Table 3 is derived from visible absorption spectra, and the formation of a hydrogen bond is supposed not to disturb that of quinhydrone, we may conclude that the energy of the hydrogen bond is not included in the heat of association given in Table 3.

Briegleb and others[9] have laid stress on the so-called "Dipolinduktions-effekt" in interpreting the association of aromatic nitro-compounds and aromatic hydrocarbons. They insisted that this dipole-induction effect, together with the dispersion force which is an intermolecular binding force working more or less between every pair of molecules, are the main causes of binding in these molecular compounds. It seems, however, that this theory cannot fully explain the intermolecular binding force of quinhydrone.

The author calculated roughly the energy contribution of the dipole-induction effect for quinhydrone based on the molecular structure shown in Fig. 1. It consists mainly of the force between the dipole of the carbonyl group of quinone (about 3.8 *D*) and that of hydroquinone induced by it, and is estimated as about -1 kcal./mol. On the other hand, the interaction between permanent dipoles of quinone and hydroquinone is estimated to be about $+0.8$ kcal./mol., and almost cancels the energy of attraction of the dipole-induction effect. Also, there seems to be no reason why

(7) M. Davies, *J. Chem. Phys.*, **8**, 577 (1940).

(8) G. Briegleb, "Zwischenmolekulare Kräfte und Molekülstruktur", Ferdinand Enke, Stuttgart, 1937, p. 104.

the dispersion force between quinone and the *B* compounds should be particularly greater than those between others which are known to make no molecular compounds.* Moreover, the dipole-induction effect, or other electrostatic interaction cannot explain the change of the absorption spectra with the formation of the molecular compounds.

Theory of electronic interaction

The measurements of the static dielectric polarization of benzene-iodine mixtures,[10] or other similar systems[11] strongly suggest that the intermolecular binding of these molecular compounds is of some kind of a coordination linkage, that is, the molecular compounds are made up of two molecules, one of which has a low ionization potential and the other has a strong electron affinity, and an electron of the former is partially transferred to the latter, forming an intermolecular covalent bond. R. S. Mulliken[12] formulated this idea using the quantum-mechanical resonance theory and explained the absorption spectra of the molecular compounds. In order to test whether this theory is applicable to the quinhydrones or not, the author made a semi-quantitative treatment of the electronic states of these molecular compounds using molecular orbital method, and compared the results with absorption data.

To proceed the theoretical analysis, it is first necessary to know the electronic states of free quinone and the free B compounds. Among the electronic orbitals of quinone and B compounds, only π-orbitals are important here because the intermolecular interaction between the σ- and inner shell orbitals of quinone and the *B* compounds are far smaller than those between π-orbitals. First, the quinone-hydroquinone system is discussed.

Quinone-hydroquinone system

The π-molecular orbitals of quinone and hydroquinone constructed by the linear combination of $2p\pi$-AO's of carbon and oxygen atoms have been calculated by Nagakura and Kuboyama[13] with a simple LCAO method, using resonance integrals and coulomb integrals which are suitably made self-consistent.** The energy levels of the MO's derived by them are given in Fig. 4. Quinhydrone belongs to the symmetry group C_{2v} in our assumed structure, and therefore there are four

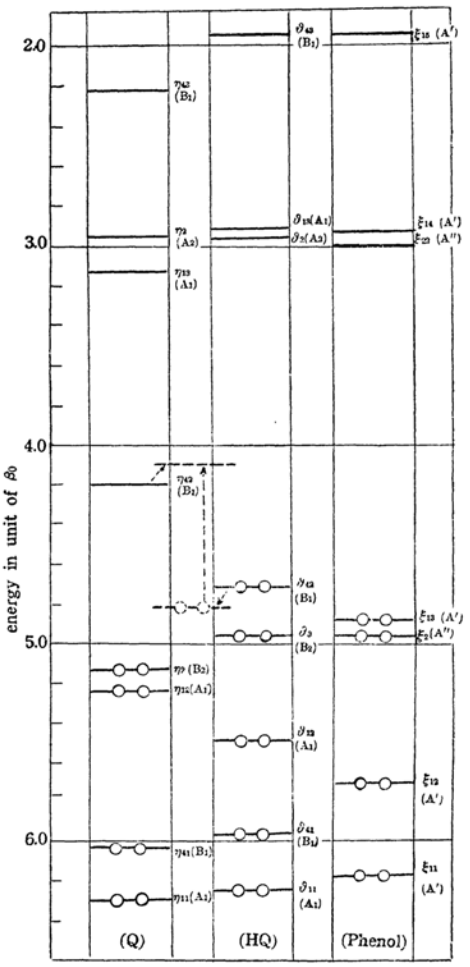

Fig. 4.—The energy levels of MO's of quinone, hydroquinone and phenol

irreducible representations A_1, A_2, B_1 and B_2.[14] The names of the irreducible representations to which each MO belongs are also given in Fig. 4. It is to be noted that the MO's of quinone and hydroquinone are very much alike since these are constructed by AO's which are similar in position as well as in number, the only difference between these two molecules being that an oxygen atom of hydroquinone has two π-electrons while that of quinone has but one. As a result, the MO of hydroquinone denoted as ϑ_{42} in Fig. 4 is a filled orbital, while the corresponding MO of quinone denoted as η_{42} is an empty one, and this difference gives slight modifications of all MO's of the one molecule as compared to the latter. Now, it can be supposed easily from experimental evidences that, relatively speaking, hydroquinone has a low ionization potential and quinone has a

* Here, we regard the dispersion force as expressible in the formula of $U=-I_1 \cdot I_2/(I_1+I_2)\times(\sigma_{1,2})\times 3/2R^6$,

(9) F. Fairbrother, *J. Chem. Soc. (London)*, **1948**, 1051.

(10) J. Weiss and H. Kronberger, *J. Chem. Soc. (London)*, **1942**, 245.

(11) R. S. Mulliken, *J. Am. Chem. Soc.*, **74**, 811 (1952).

(12) S. Nagakura and A. Kuboyama (*unpublished results*).

** The same method was used in the calculation of the energy levels of furan, pyrrole and thiophen. See, "S. Nagakura and T. Hosoya, This Bulletin, **25**, 179 (1952)".

(13) Here the notations are the same as those used by Eyring et al. See, "Eyring, Walter and Kimball, Quantum Chemistry, Appendix VII". The operation σ_v is taken as the reflection in the plane including four oxygen atoms.

strong electron affinity. This corresponds to the fact that the difference between the energies of ϑ_{42} and η_{42} is small. (See, Fig. 4). In addition, these two orbitals belong to the same irreducible representation in the over-all symmetry of the molecular compound. From these facts, it can be seen that an intermolecular conjugation between ϑ_{42} and η_{42} (which results an partial migration of an electron that is originally occupying ϑ_{42} to η_{42}) is easily produced. And, in the first approximation, only the consideration of this conjugation is sufficient in the treatment of the intermolecular conjugation as a whole.

The reason for this is given briefly as follows: Since migration is possible only between two MO's belonging to the same irreducible representation, we can see that the following intermolecular migrations of electrons from hydroquinone to quinone may be possible,

$$\vartheta_{42}\rightarrow\eta_{43},\ \vartheta_{41}\rightarrow\eta_{42},\ \vartheta_{12}\rightarrow\eta_{13},\ \text{etc.}$$

But these migrations are thought to be far less possible than that of $\vartheta_{42}\rightarrow\eta_{43}$, because in such cases the energy difference between MO's are much greater than that between ϑ_{42} and η_{42}. Next, we should note that intermolecular conjugations may occur between two filled orbitals of hydroquinone and quinone, e. g., ϑ_3 and η_3, ϑ_{12} and η_{12} etc. However, such conjugations between filled orbitals produce no effect but an increase of total electronic energy, which, as Parr and Mulliken have pointed out,[14] is attributable to the exchange repulsion between molecules.

Now we can set up the total electronic wave function of quinhydrone in the ground state as an anti-symmetrized product of one-electron MO's.

$$\begin{aligned}\Psi_g = n_g(18!)^{-1/2}\sum_{\nu}(-1)^{p}\,\mathrm{P}\,&\eta_{11}(1)\eta_{11}(2)\eta_{12}(3)\eta_{12}(4)\\ &\cdots\cdots\vartheta_{11}(9)\vartheta_{11}(10)\vartheta_{12}(11)\vartheta_{12}(12)\ \cdots\cdots\\ &\phi_g(17)\phi_g(18)\times\alpha_1\beta_2\alpha_3\beta_4\cdots\cdots\alpha_{17}\beta_{18} \qquad (4)\end{aligned}$$

$$\phi_g(\nu) = a_0\vartheta_{42}(\nu) + b_0\eta_{42}(\nu) \qquad (5)$$

Since a complete treatment of the MO's including eighteen electrons is extremely difficult, we are ought to be satisfied by a simple approximation in which the energy of the migrating electrons is expressed as

$$E(\nu) = \int \phi(\nu) H_\nu \phi(\nu) d\tau_\nu \qquad (6)$$

Here, H_ν is the total hamiltonian for the migrating electron including the kinetic energy operator of an electron, the potentials of atomic cores and other electrons. Then, the minimization of $E(\nu)$ leads to the secular equation,

$$\begin{vmatrix} W_{42}-E & \beta \\ \beta & W'_{42}-E \end{vmatrix} = 0 \qquad (7)$$

where W_{42} and W'_{42} are the coulomb integrals of the MO ϑ_{42} and η_{42}, respectively, and β is the resonance integral over them. Solving (7), we get the lower and upper roots, E_g and E_e;

$$E_{g,\,e} = (W_{42}+W'_{42})/2 \pm \{(\Delta W/2)^2+\beta^2\}^{1/2} \qquad (8)$$

in which, $\Delta W = W'_{42}-W_{42}$. a_0 and b_0 can be immediately calculated from E_g. We get another wave-function ϕ_e corresponding to the upper level, E_e. This is approximately given by the following formula.

$$\phi_e = b_0\vartheta_{42} - a_0\eta_{42} \qquad (9)$$

As is shown lately, a_0 is nearly one and b_0 is far smaller than a_0. Hence, it can be said that ϕ_g is much alike to ϑ_{42} and ϕ_e is much alike to η_{42}. Therefore, if we assign the visible absorption of quinhydrone to the transition from ϕ_g to ϕ_e, it has the character of an intermolecular charge-transfer spectra and agrees with Nakamoto's experimental results (ref. (2)). Other transitions of this molecular compound which have the electric moment normal to the benzene rings cannot be found in this region of wave length.

Next, we will calculate the transition moment of this transition. The total electronic wave function of quinhydrone in the singlet excited state is given in a way similar to (4).

$$\begin{aligned}\Psi_e = n_e(18!)^{-1/2}\sum_{\nu}(-1)^{p}\,\mathrm{P}\,&\eta_{11}(1)\eta_{11}(2)\eta_{12}(3)\eta_{12}(4)\\ &\cdots\cdots\vartheta_{11}(9)\vartheta_{11}(10)\vartheta_{12}(11)\vartheta_{12}(12)\ \cdots\cdots\\ &\phi_g(17)\phi_e(18)\times\alpha_1\beta_2\alpha_3\beta_4\ \cdots\cdots\\ &(2)^{-1/2}(\alpha_{17}\beta_{18}-\alpha_{18}\beta_{17}) \qquad (10)\end{aligned}$$

The transition moment μ is, for definition, given by

$$\mu = e\int \Psi_e^*\Big(\sum_{\nu} x\Big)\Psi_g d\tau \qquad (11)$$

As a result of calculation, μ is approximately given by

$$\mu \doteqdot e a_0^2 b_0 R/\sqrt{2} \qquad (12)$$

in which R being the distance between two molecules. From (8), we can see that a_0 and b_0 depend on β and ΔW. Since resonance integrals are in many cases proportional to the corresponding overlap integrals, we calculated the overlap integral between ϑ_{42} and η_{42} in order to know the magnitude of β. This can be expanded in terms of overlap integrals between AO's and can be easily calculated. If we use Slater type AO's with screening constants $z_c=3.25$, $z_o=4.55$, the result was 0.043. Then, we calculate β from the resonance integral β_0 and the overlap integral s_0 between two adjacent carbon atoms of benzene in the following way,***

(14) Parr and Mulliken, *J. Chem. Phys.*, **19**, 1273 (1951).

*** Such a procedure is often used in the calculation of the resonance integrals between two π-orbitals. Though we are here dealing with resonance integrals between two σ-orbitals, the situation is conceivable to be nearly the same.

Table 3

(The unit of W's is in β_0)

ΔW	$\Delta E(=E_e-W'_{42})$	a_0	b_0	μ_{calc}	E_e-E_g	f_{obs}	μ_{obs}
$\beta=0.2\ \beta_0$							
0.5	0.070	0.945	0.331	2.94 D	0.64 (6800 Å)	0.014	1.14
0.7	0.055	0.963	0.265	2.49 D	0.81 (5370 Å)		
0.9	0.044	0.978	0.216	2.13 D	0.99 (4390 Å)		
1.1	0.035	0.985	0.172	1.73 D	1.17 (3720 Å)		
$\beta=0.1\ \beta_0$							
0.9	0.012	0.992	0.119	1.22 D	0.92 (4740 Å)		

$$\beta=\beta_0\times s/s_0$$

we get $\beta=0.17\ \beta_0$. It was suggested by Mulliken and others that the overlap integral between bonded atoms or molecules is supposed to be greater than that which is calculated from the Slater AO's. Therefore, in this case, we tentatively assume that β is the order of $0.20\ \beta_0$. The estimation of ΔW is also difficult. But, fortunately, the variation of this does not influence the transition moment significantly. We estimated that it lies in a region from 0.5 to $1.0\ \beta_0$*, and calculated various a_0, b_0 values using various ΔW in this region. From these values, the transition moment μ can be calculated. On the other hand, experimental oscillator strength was calculated from the absorption data in solution using the following formula,

$$f_{obs}=(nc^2m/N\pi e^2)\times 10^3\int \varepsilon d\nu^{(15)}\fallingdotseq 0.1875\times 10^{-8} n\varepsilon_{max}\cdot\Delta\nu \quad (13)$$

in which n is the index of refraction of the solution and $\Delta\nu$ is the distance between two points in the absorption curve at which the intensity is half the maximum value. Applying the Lorentz-Lorenz correction to this,[16] we can get f_{obs} in gaseous state, and from it the μ_{obs} can be calculated. The calculated and experimental μ's are given in Table 3. The transition energy depends mainly on ΔW, and the value of ΔW which gives a transition energy most close to the experimental one is seen to be $0.9\ \beta_0$. For reference, the oscillator strengths using $\beta=0.10\ \beta_0$ are also given using $\Delta W=0.9\ \beta_0$. These results show that the charge transfer spectra proposed here may have sufficiently strong oscillator strength to be correlated with the values experimentally obtained.

Although it is dangerous to refer to the total π-electronic energy of the molecular compound from the simple MO theory, it can be supposed that this intermolecular conjugation between filled and unfilled MO's will produce a decrease of electronic energy. If this is true, such a decrease of electronic energy by intermolecular conjugation will be the most characteristic part of the intermolecular binding energy of these molecular compounds.

Other quinhydrone-type molecular compounds

The π-electronic state of dimethylhydroquinone is quite similar to that of hydroquinone. Hence, we can expect that the π-electronic interaction between quinone and dimethylhydroquinone is also quite similar to that of quinone-hydroquinone system. From the experimental results shown in Part I., it can be seen that the molecular compound of dimethyl hydroquinone has a considerably lower absorption intensity and binding energy than that of hxdroquinone. This can be understood in the following way. The intermolecular distance of this molecular compound is supposed to be made larger than in the case of hydroquinone because the methyl group will considerably increase the steric repulsion between molecules. The resonance integral between ϑ_{42} and η_{42} will become smaller owing to the large intermolecular distance, and this will decrease the intensity of the charge transfer spectra and the charge transfer force.

In order to discuss the case of quinone-phenol molecular compound, we should know the electronic state of phenol. The author calculated the LCAO MO energy levels of phenol by use of the same method as was adopted in the calculation of quinone and hydroquinone. The energy levels obtained are given also in Fig. 4. We assume that the symmetry group of quinone-phenol molecular compound is C_{1h} (see, ref. (14)), that is, it has only one plane of symmetry (xz plane in Fig. 1). The names of the irreducible representations to which the MO's of phenol belong in the overall symmetry of the molecular compound are given in Fig. 4. On the other hand, the irreducible representations of the MO's of quinone written in Fig. 4 are transformed in this case in the following way,

$$A_1,\ B_1 \rightarrow A',\quad A_2,\ B_2 \rightarrow A''.$$

As a result, the highest filled MO of phenol, ξ_{13}, and the lowest unfilled MO of quinone, η_{42}, belong to the same irreducible representation in the C_{1h}

* The ΔW calculated as the energy difference between γ_{42} and δ_{42} in Fig. 4 is $0.5\beta_0$. On the other hand, the electron affinity for η_{42} orbital was calculated to be about 8.0 ev., with a method similar to that employed by Sklar[16] in the calculation of the electron affinity of benzene ring of substituted benzens. This corresponds roughly to $\Delta W=1.0\beta_0$.

(15) A. L. Sklar, *J. Chem. Phys.*, **7**, 992 (1939).

symmetry of the molecular compound. From the stand-point analogous to that in the former discussions, we may conclude that, in this molecular compound, the conjugation between ξ_{13} and η_{42} is predominant. By the calculation of the AO coefficients of the MO's of phenol, we can see that the AO coefficients of ξ_{13} are very much like those of ϑ_{42} in hydroquinone and therefore it is conceivable that the overlap integral between ξ_{13} and η_{42} is of nearly the same magnitude as that between ϑ_{42} and η_{42}. The calculated value of the former integral is really 0.040, in close agreement with the latter. Hence, we may expect that the resonance integral between ξ_{13} and η_{42} is also as large as that between ϑ_{42} and η_{42}. The ionization potential of phenol is supposed to be larger than that of hydroquinone, because the energy level of the highest filled orbital of phenol is lower than that of hydroquinone. Hence, ΔW in quinone-phenol system is expected to be larger than that of quinone-hydroquinone system. The change of ΔW, however, does not influence the absorption intensity seriously as was previously stated. Therefore, we deduce that the absorption intensity of quinone-phenol system is of the same order of magnitnde with that of quinone-hydroquinone system. Also, the charge transfer force as a contribution of the binding energy in this molecular compound is expected to be the same as quinone-hydroquinone system. However, as the change of ΔW directly changes the transition energy, we should expect that the peak wave-length of quinone-phenol system will be shorter than that of quinone-hydroquinone system. These considerations agree with experimental results.

Summary

The absolute intensities of the visible absorption spectra and the binding energies of quinhydrone-type molecular compounds have been determined by the measurements of their absorption intensities in solutions. The visible absorption spectra of these molecular compounds can be explained as the charge-transfer spectra of the π-electrons of quinone and the B compounds. The intensity of these charge-transfer spectra can be calculated roughly by setting up linear combination of the lowest unfilled MO of quinone and the highest filled MO of the B compound, and the results agree qualitatively with the experimentally derived absorption oscillator strengths. This charge-transfer resonance is thought to be the most characteristic part of the intermolecular binding energy in these molecular compounds.

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