Physico-chemical Studies on Molecular Compounds. IV. Heats of Solution of Crystalline Quinone, Hydroquinone and Quinhydrone into Acetone and Heat of Formation of Crystalline Quinhydrone

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Introduction

Although there have appeared already numerous investigations on the crystalline molecular compounds from the standpoint of organic chemistry in crystalline states, physico-chemical studies concerning the interaction energies between component molecules are very scanty in comparison with those in solution. The heat of formation of the molecular compound in solution, however, involves ambiguous energy quantities referring to the solvation energy, the accurate estimation of which is difficult on account of the unknown relative molecular arrangement.

On the other hand, during the past several years, a considerable number of complete crystal structure determinations of molecular compounds have been performed, so that it is much more suitable to determine the interaction energies of these materials. For this purpose, we have determined in a previous report,[1] indirectly the interaction energy of quinhydrone, its crystal structure being completely determined in this laboratory[2]. In the present investigation, we have undertaken to determine this energy more accurately by direct measurements of heats of solution of quinhydrone as well as those of component crystals.

Experimental

a) Apparatus and procedures.—The calorimeter used for the present work is in principle identical with that reported in a previous paper[3]. A few points improved now are as follows:

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[1] I. Nitta, S. Seki, H. Chihara and K. Suzuki, *Sci. Paper Osaka Univ.* No. 29 (1951).

[2] I. Nitta, K. Osaki and H. Matsuda (to be published).

[3] S. Seki and K. Suzuki, This Bulletin, **26**, 63 (1953).

i) In order to hold the constancy of temperature of the thermostat more accurately, the whole apparatus was surrounded by an air thermostat, the temperature of which was controlled within the accuracy of 0.1~0.2°C and held ca. 0.2°C below the temperature of the water thermostat. For the regulation of temperature of the inner water jacket, five helical glass tubes of ordinary toluene regulators were connected in parallel (ca. 400 cc.) and the portion of mercury-platinum contact was dipped into the water in order to avoid the temperature fluctuation of the outer atmosphere.

As the results of these improvements the temperature of the inner water jacket was held to be constant within the accuracy of 0.0001°C.

ii) Instead of the precision type voltmeter and ammeter used previously for the determination of water equivalent of the calorimeter, Yokogawa P-7 type low voltage potentiometer and potential divider (resistance, 29330 ohm; magnification, 99.708 : 1) were used for the measurement of voltage drop of the calorimeter heater, and the current through the heater was calculated by the measurement of the potential drop of manganin standard resistance (9.9967 ohm at 25°C, immersed in special transformer oil) connected in series with the heater. As the change of resistance of the standard resistance and potential divider due to Joule's heat was very small, its effects can be ignored. The correction for the amount of current through the circuit of the potential divider was taken into consideration. The circuit for the determination of water equivalent is shown in Fig. 1.

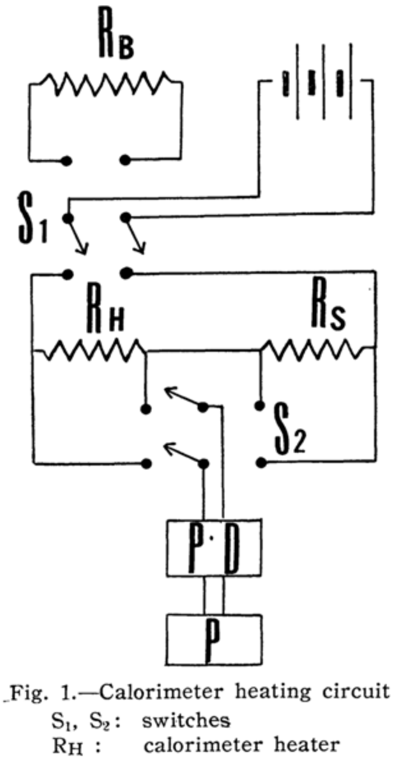

Fig. 1.—Calorimeter heating circuit

S_1, S_2 : switches
R_H : calorimeter heater
R_S : standard resistance
R_B : ballast resistor
P : potentiometer
PD : Potential divider

iii) For the accurate determination of the heat of solution of crystalline materials, it is very desirable to dissolve a specimen as quickly as possible into the solvent. For this purpose, we have chosen acetone as the solvent. As a dissolving device, we have adopted the method of breaking a thin glass bulb (capacity: ca. 2 c.c.) containing a powdered specimen. In this way, about 80% of the samples dissolve within fifteen seconds and the whole process of dissolution was accomplished within about three minutes. The endothermic effect due to the evaporation of acetone into the air bubbles liberated from the glass bulb was calibrated before the experiment and found to be expressed approximately by the following relation;

$$\Delta H_b = 0.10 \times v \text{ cal}$$

ΔH_b : heat absorbed,
v : empty space of the bulb in cc.

b) Samples

i) *Hydroquinone* (*Hq*): The product of Wakô Pure Chemicals Ltd. was recrystallized twice from ethyl alcohol and then subjected to fractional sublimation under high vacuum (10^{-5} mm. Hg) at 100°C. (Melting point: 172.5~173.0°C.) This material has three modifications[4] (α, β and γ). The material obtained by this operation was ascertained to be of the α-form by taking the Debyephotograph. To exclude the possibility of coexsistence of the minute amount of the γ-form, the sample was powdered in agate mortar and stored for about four months in a vacuum desiccator.

ii) *Quinone* (*Q*): *Hq* prepared as mentioned above was oxidized by sulfuric acid and aqueous solution of $K_2Cr_2O_7$, then recrystallized from benzene and ligroin, and finally subjected to fractional sublimation under high vacuum at room temperature using solid carbon dioxide as the cooling material. (Melting point: 115.0~115.5°C.)

iii) *Quinhydrone* (*QH*): Equimolar *Q* and *Hq* prepared by the above mentioned methods are dissolved into acetone. Then this solution was evaporated gradually at room temperature for about one day. The precipitated *QH* at the bottom of the beaker was stored in a darkened desiccator together with pure *Q* in order to prevent frac-

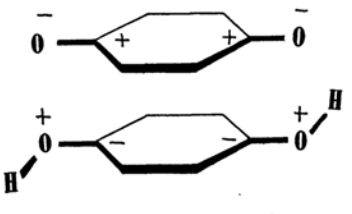

Fig. 2.—A model for quinhydrone by Murakami

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[4] W.A. Caspari, *J. Chem Soc.* **129**, 2944 (1926); **131**, 1093 (1927) H.M. Powell and P. Riesz, *Nature* **161**, 52 (1948).

tional evaporation[1] of Q from the QH crystals. (Melting point: 169.5~170.0°C C.*)

Results and Discussion

a) Experimental results.—All measurements were carried out at about 24°C and their results are given in Table 1. As the solvent for the determination of the heat of solution of Q, pure acetone as well as acetone solution already containing equimolar Hq were used to see if the molecular compound formation be possible in the solution. As is shown in the table, two values of heats of solution for these solvents were equal within the experimental error.

Table 1

Heats of solution of QH, Hq and Q

Sample	Exptl. No.	m	N	t°C	ΔH kcal/mol.
Quinhydrone	1	0.01384	494	24.02	9.142
	2	0.01373	499	24.03	9.179
	3	0.01393	491	24.14	9.119
	Average				9.147±0.012
Hydroquinone	4	0.01394	491	24.06	−0.380
	5	0.01439	476	24.10	−0.358
	Average				−0.369±0.008
Quinone*	6	0.01435	477	24.00	4.157
	7	0.01399	490	23.98	4.100
	Average				4.129±0.022
Quinone	8	0.01394	491	23.98	4.114±(0.02)

m: mole number of the sample used.
N: mole number of acetone to dissolve one mole of solute.
t°C: average temperature of the measurement.
ΔH: +sign is taken for the endothermic process.
*: for the solvent containing equimolar Hq.

b) Heat of solvation of quinone and hydroquinone. Energy of hydrogen bond between acetone and hydroquinone.—Prior to the discussions on the problems of molecular compound formation, the solution state of each component will be discussed here. As is well-known, the heat of solvation at infinite dilution ΔH^{∞}_{soln} is given by the following equation

$$\Delta H^{\infty}_{solv}=\Delta H^{\infty}_{soln}-\Delta H_{sub}$$

where ΔH^{∞}_{soln} is the heat of solution at infinite dilution, ΔH_{sub} the heat of sublimation of the crystals. The heat of solution obtained by the present investigation correspounds to that at a finite concentration, so that the heat of dilution brought to the infinite dilution should be added over this experimental value to evaluate ΔH^{∞}_{soln}. As for the heat of dilution of Hq, it is guessed to be less than 100 cal/mol. from the considerations of the data of heats of dilution[5] of aqueous solution at the concentrated state in connection with the data on the degrees of association of phenol in nonpolar solvent determined by infra-red absorption spectra[6]. Presumably this correction factor is much less for Q. Since the orders of magnitudes of these corrections are smaller than or equal to the experimental errors of the heats of sublimation, it may be approximately correct to substitute ΔH_{soln} (under experimental condition) for ΔH^{∞}_{soln} for the present discussion. ΔH^{∞}_{solv} in Table 2 were calculated on this assumption by use of the heats of sublimation measured by us.[1] In the table also the values for aqueous solutions and that of resorcinol are given for reference.

There exists evidently considerable difference between the heats of solvation for acetone of Hq and Q, respectively, as seen in the table. This fact may be explained in the following way:

Considering the process of dissolution of a molecule into a solvent, heat of solvation of a molecule consists of the following two parts;

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* The samples preciptated from aqueous or alcoholic solutions, the products prepared from the melts of the equimolar components, the product of Kahlbaum Co., etc. exhibit lower melting points as well as wider melting ranges than the sample mentioned above.

5) "International Critical Table."

6) W. Lütcke and R. Mecke, *Z. Electrochem*, 53, 241 (1949).

namely, (I) the heat necessary to create a cavity which holds a solute molecule in solvent (endothermic) and (II) the heat evolved due to the interaction between a solute molecule and surrounding solvent molecules. Of these two, the former may be looked upon to be approximately equal for *Q* and *Hq*, because of their nearly equal size and shape. Hence, the difference should be attributed to the second effect, of which van der Waals interaction between solvent and solute molecules may be also nearly equal. Accordingly, the difference 9.64 kcal/mol. should be attributed to the hydrogen bond formation of O-H······O=C type as shown in Fig. 3, whereas the *Q* molecule does not form such a hydrogen bond.

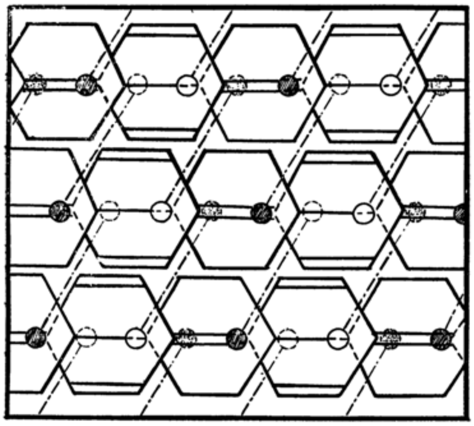

Fig. 3.—A schematic representation of molecular packing in quinhydrone crystal

Hatched circles: oxygen atoms of quinone
White circles: oxygen atoms of hydroquinone
——•——•——: hydrogen bonds

In general, the energy of hydrogen bond determined in a solution state has always some ambiguities, as the estimation of the differece of the solvation energies of associated and non-associated molecules is difficult. In the present case, however, they are cancelled empirically by the solvent effect of *Q* molecule having nearly equal size, shape and numbers of electrons. The energy of hydrogen bond $\frac{1}{2}(9.64)=4.82$ kcal/mol determined is somewhat smaller than that of formic acid dimer[7] (6.3 kcal/mol.) having similar type of hydrogen bond (O—H······O=C). This small difference may be attributed to the weaker proten donating power of hydroquinone and to the weaker proton accepting power of acetone molecule.

The smaller difference between the heats of hydration of *Q* and *Hq* (5.35 kcal/mol: see Table 2) in comparision with that of heats of solvation for acetone indicates a possibility of hydrogen bond formation of *Q* molecule in aqueous solution where the water molecules play a dual role of proton donor as well as of proton acceptor. For the quantitative ex-

Table 2

Heats of solution, hydration, solvation and related data of *Hq*, *Q* and resorcinol. unit: kcal/mol.

Substances		Water		Acetone	
	ΔH_{sub}	ΔH_{soln}	ΔH_{hyd}	ΔH_{soln}	ΔH_{solv}
Quinone	16.38±0.14 (a)	4.69 (c)	11.69	4.11	12.27
Hydroquinone	21.54±0.22 (a)	4.50 (d)	17.04	−0.37	21.91
Resorcinol	22.8 ±0.4 (b)	4.0 (e)	18.8	—	—

a: See reference (1)
b: K.L. Wolf and H.G. Trieschmann, *Z. physik. Chem.*, B 27, 37 (1934).
c: Schreiner, 4.69 kcal at room temp. N=1830;
d: Schreiner, 4.50 kcal at room temp. N=360. (sample crystallized from glacial acetic acid), 4.56 kcal at room temp. N=360 (sample sublimed at ordinary pressure); Kolossowsky, 4.46 kcal at 16°C, N=282; We have adopted average value of Schreiner and that of Kolossowsky.
e: Robertson and Ubbelohde, 4.12 kcal at 18°C N=410 (α-modification), 3.90 kcal at 18°C N=410 (β-modification); We have adopted the average of their values.

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[7] As to the estimation of hydrogen bond energy of formic acid dimer, see I. Nitta, S. Seki and K. Suzuki, This Bulletin **24**, 64 (1951).

planation of this difference, however, further informations on the nature of proton accepting power of the phenol derivatives may be neccessary[8].

c) Molecular compound formation.—Now, we should like to proceed to the problem of molecular compound formation. According to many physico-chemical investigations carried out hitherto,[9] the following chemical equilibrium;

$$QH \rightleftharpoons Q + Hq$$

in water, alcohol and liquid ammonia is always largely shifted to the right hand side at room temperatures, and the amount of QH molecules is only 6% even at the saturated solution. Therefore, in the case of dilute solution where the present work was done*, the amount of QH would be considered to be negligible. Indeed, in the present experiment, the fact that the heat of solution of Q for pure acetone is equal to that for acetone solution containing equimolar Hq within the experimental error (ca. 20 cal.) is concordant with this expectation.

On the basis of these discussions given above and from the data of heat of solution, we are now in a position to calculate the heat of formation of QH crystals from the component crystals at 24°C. The heat of formation at 0°K. can also be estimated employing the specific heats data measured by Lange[10]. These two values together with the corresponding changes of entropy and Gibbs free energy which are calculated by assuming the validity of the third law of thermodynamics, are all given in Table 3. In the Table, the heats of formation of QH (the first row) calculated from other thermodynamic investigations are also given for reference. Of these the second one (4.7 kcal.), which was estimated from our previous investigation on the vapor pressure of Q, Hq and QH[1], is nearly equal to the value determined directly in this work. Also the same quantities determined from the electrode potential etc., and from the heats of combustions are given. As they are derived from the difference of several thermodynamic quantities, they cannot be free from considerable error. The heat of sublimation of QH (43.31 kcal in the last row), which cannot be estimated accurately from the vapor pressure measurement*, was determined directly by the summation of heats of sublimation of each component crystals (21.54 kcal. for Hq and 16.38 kcal. for Q) and heat of formation of QH (5.386 kcal.).

Table 3

Some thermochemical data of crystalline quinhydrone

ΔH_{form} at 24°C	-5.387 ± 0.042 (-4.7 ± 1.0, (a) -8.1 ± 2.1, (b) $-4.3 \pm ?$ (c))
ΔH_{form} at 0°K	-5.26
ΔG_{form} at 24°C	-3.67
ΔS_{form} at 24°C	-6.28
ΔH_{sub}	43.31 ± 0.42

unit: energy, in kcal/mol.
entropy in e.u/mol.

a: value estimated from vapor pressure. see ref. (1)

b: value estimated from heat of combustion. These data are taken from the following; Quinone: 654.8 (Berthelot, Louginin); 659.2 (Berthelot, Recoura); 656.6 (Schreiner, Berner); 656.3 (Swietoslawsky from Valeur's data); average value 656.7±0.6 Hydroquinone: 685.9 (Berthelot, Louginin); 685.8 (Stohnann, Langbeim); 684.7 (Baker); 684.0 (Swietoslawsky); 682.6 (Berner, Schreiner); average value 684.6±0.4 Quinhydrone 1331.5 and 1334.8 (two different samples, Berner, Schreiner); average value 1333.2±1.1.

c: value estimated from electrode potential, specific heats and third law by Schreiner.

Finally, a few words may be added here on the heat of formation of QH. Our result (5.386 kcal./mol.) is considerably different from the heat of formation of QH in aqueous solution (2.35 kcal.) determined by Berthoid.[9b] The discrepancy, however, is a matter of course, since our value is for the crystalline state and the latter for the aqueous solution state in which the hydration process plays a complex role**.

d) Nature of intermolecular forces in

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[8] In the case of aliphatic alcohols, we have analysed this problem somewhat more in detail. see ref. (3).

[9] a) Vapor pressure depression of ammonia solution: I. Shaltenstein and A.M. Monoszon, *Z. Phys Chem.*, **A165**, 147 (1933).
b) Solubility in acqeous solution: A. Berthoid and S. Kunz, *Helv. Chim. Acta.* **21**, 17 (1938).
c) Absorption spectra in aqueous and alcoholic solutions: L. Michaelis and S. Grannick, *J. Am. Chem. Soc.*, **66**, 1023 (1944).
d) Diamagnetic susceptibility: L. Michaelis, M.P. Schubert, R. K. Reber, J. A. Kuck and S. Grannick, *J. Am. Chem. Soc.* **60**, 1678 (1938).

[*] Judging from the heat of dissociation of QH (2.35 kcal/mol) measured by Berthoid et. al. (9b), the amount of QH may be less than 1% at the present experimental condition.

[10] The values of Lange are put in order by Schreiner, *Z. phys. Chem.*, **117**, 57, (1925).

[*] The value given in a previous paper corresponds to the decompositional sublimation to form 95% Q vapor and 5% Hq vapor and leave α-Hydroquinone as a residue.

[**] The solvent effects for the heat of formation of (1:1) molecular compounds between trinitrobenzene and naphthalene (or anthracene) are known from the spectroscopic measurements of Briegleb et. al.; *Z. physik. Chem.*, **B19**, 255 (1932).

crystalline *QH*.—We may now discuss the nature of intermolecular forces on the basis of our experimental results. As regards the origin of these intermolecular forces of *QH*, there have been already put forward several explanations. These are:

i) ordinary covalent bond.
ii) ionic binding: i. e. the electrostatic coulombic attraction between ions. (Q^+Hq^- or Q^-Hq^+)
iii) coupling of two semiquinones.
iv) hydrogen bond.
v) a) dispersion forces.
  b) dipole or multipole interactions.
  c) induction forces.
  d) charge transfer forces, etc.

The first theory of ordinary covalent bond is excluded by the two facts that the magnitude of interaction energy (5 kcal.) is too small to be an ordinary covalent bond energy and that the intermolecular distances which have been determined by the X-ray method are very much longer than the sum of covalent radii.

The second ionic binding theory can not explain the small amount of heat of sublimation which is in same order to those of ordinary molecular crystals. The magnetic property of this crystal also disagrees with the complete ionized structure, for the odd electron configuration of molecules should exhibit the paramagnetic effect, whereas this crystal actually is diamagnetic[11]. The explanation of ionic binding by Weiss et al. based on the non-additivity of molar polarization of *QH* from those of the components is not always conclusive for the evidence of the ionic structure of component molecules[12].

The third one, the semiquinone theory disagrees also wrth the fact of diamagnetic property of *QH*.

As regards the fourth, *Hq* and *Q* molecules are really combined with each other by hydrogen bond as shown in Fig. 3. Although the crystal structure of *α-Hq* is not yet known, it is quite likely that these molecules in crystals would be also linked together by hydrogen bonds, in some analogy to the crystal structure of *β-Hq*, *α* or *β*-resorcinol and phlorogrucinol, in each of which hydrogen bonds combine these molecules.

The energy of hydrogen bond ($C=O\cdots\cdots H—O$) in *QH* crystal will be estimated from the values of formic acid dimer (6.3 kcal.) or of acetone·*Hq* associate (4.8 kcal). On the other hand, the energy of hydrogen bond of *Hq* can be taken to be about 4.0 kcal./mol. by the comparison of the heat of sublimation of *Hq* with that of *p*-Xylene[13]. Hence, the contribution of hydrogen bond energy for the molecular compound formation is estimated to be from 4.6 to 1.6 kcal. (12.6—8.0) or (9.6—8.0). Although the color effect of *QH* would not be explained essentially by this effect, the hydrogen bond formation would contribute to a certain extent for molecular compound formation. As shown in Table 4, the facts that the molar ratios of molecular compounds I, II, III and IV groups are parallel with the numbers of hydrogen atoms in hydroxyl or amino groups and that there can not be formed stable crystals of molecular compounds in the combinations of V, VI, VII and X groups having no hydroxyl groups, suggest a role of hydrogen bond for the molecular compound formation. However, it may be safely said that this effect is not a very decisive one, as is evidently seen in the cases of VIII, IX and X.

Table 4

Crystalline molecular compounds between quinone and other substances (*B* component)

Group	Substances	Molar ratio $Q:B$
I	phenol, *o*-, *m*-, *p*-cresol, hydroquinone methy ether	1 : 2
II	hydroquinone, *p*-toluidine, *p*-nitroaniline	1 : 1
III	resorcinol, pyrocatechol, *α*-, *β*-naphthol	1 : 1 and other ratio
IV	(a) pyrogallol, (b) phenylenediamine	(a) 3 : 1 (b) 2 : 1
V	*o*-, *m*-nitroaniline	None
VI	hydroquinone dimethyl ether	None
VII	benzene, toluene, xylene, naphthalene, tolane, azobenzene, nitrobenzene	None
VIII	anthracene	1 : 1
IX	phenanthrene	1 : 6
X	aliphatic hydrocarbons, ethers, aldehydes ketones	None
XI	aliphatic alcohols, acids, amides	None

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[11] S. Banerjee, *Z. Krist.*, **100**, 316 (1939); H. Mikhail and F.G. Baddar, *J. Chem Soc.*, **1944** 540

[12] The disagreement between the molar polarization of *QH* and the sum of those for component crystals may be also explained by the anisotropy of electron distribution and by the change of atomic polarizability caused by hydrogen bond formation. Indeed, the other crystals measured by them which deviate remarkably from the additivity involves the $N-H\cdots O$ or $O-H\cdots O$ hydrogen bonds. See: J. Weiss, H. Kronberger, *J. Chem. Soc.*, **1944** 464.

[13] Heat of sublimation of *p*-Xylene: 13.5 kcal/mol., Linder's value from Landolt-Börnstein's Table.

Next, we proceed to the fifth. The ordinary dispersion effect has not been hitherto taken nto consideration at all, since it can not explain the reasons, why the compound formation takes place between a pair of specified molecules and also why such a remarkable change of color[14] accompanies this process. Indeed, this effect may be ignored, in the case of a compound formation in solution, but it is worth while to reexamine it for the case of crystalline state where the packing of molecules plays a much more important role than in the case of solution state, as the dispersion forces are sensitive to the mode of molecular packing. For example, the difficulty of compound formation between aliphatic and aromatic molecules (see examples X and XI in table 4), the non-existence of crystalline molecular compounds of the systems such as I_2-benzene, and tetranitromethane-diphenylmethane (typical examples of molecular compounds in solutions) may be attributed to the unfavourable packing of component molecules because of the considerable difference of their sizes and shapes.

As a measure of the dispersion energy contribution for the heat of sublimation of the *QH*, twice the heat of sublimation of *p*-Xylene (isoelectronic molecule to *Q* and *Hq*) may be tentatively adopted. Then, it is found that the contribution of the dispersion energy to the heat of sublimation is estimated to be about 60% of the total and that the sum of this contribution and the hydrogen bond energy estimated above is not yet sufficient to explain the total observed (see Table 5). The facts that the density of *QH* (1.41) is larger than those of *Q* (1.32) and *Hq* (1.33) and that the nearest intermolecular[2] distance between *Hq* and *Q* molecules lying parallel in *QH* crystal (3.2A) is abnormally shorter than those of any aromatic compounds, suggest also there are partaking other sorts of attraction forces between component molecules.

Table 5

Contribution of the various kinds of energy to the heats of sublimation of *Q*, *Hq*, and QH, and to the heat of formation of *QH*.
(unit: kcal/mol.)

	Heat of sublimation			Heat of Formation
	Hq	*Q*	*QH*	
Total	21.54	16.38	43.31	5.386
Hydrogen bond	8.0	0	12.6 ～ 9.6	4.6 ～ 1.6
Dispersion	13.5	13.5	27	0
Others	0	2.9	3.7 ～ 6.7	0.8 ～ 3.8

Recently, Murakami[15] put forward a theory for the intermolecular forces of *QH* type molecular compounds. From the point of view of resonance theory, he supposed the π-electron charge distributions of *Q* and *Hq* as shown in Fig. 4. If we assume to put *Hq* molecule just upon *Q* molecule in a parallel position as shown in the figure, the charges of opposite signs in respective molecules come to the nearest, so that we can expect there will arise strong electrostatic attraction between them. He postulated this is the cause of the molecular compound formation, and also explained qualitatively the shift of absorption band to the longer wave length as well as the simultaneous intensity increase of the band. His theory is, however, of qualitative nature, so we have attempted here to evaluate the π-electron charge distribution semi-quantitatively. Assuming the molecular symmetry of *Hq* molecule approximately to be D_{2h} the electron charge density[16] of *Hq* molecule was computed by the simple LCAO-MO theory. In this case, the coulombic integrals of oxygen and adjacent atoms as well as the resonance integrals between oxygen and adjascent atoms were calculated by the use of Jaffe's parameter for phenol[17], all the overlap integrals being ignored. The results obtained as well as the corresponding values for *Q* obtained by Coulson et al.[18] are

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[14] The absorption spectra of *QH* in crystalline state: K. Nakamoto, *J. Am. Chem. Soc.*, **74**, 1739 (1952).

[15] H. Murakami, *Sci. Paper Osaka Univ.* No. 18 (1949).

[16] C.A. Coulson, H.C. Longuet-Higgins, *Proc. Roy. Soc.*, A **192**, 16 (1947).

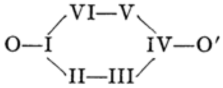
[17] H.H. Jaffe, *J. Chem. Phys.* **20**, 279 (1952).

[18] C.A. Coulson, Valence p. 256 (Oxford Univ. Press. 1952). [After completion of this work, we became aware of the similar calculations on *Q* by Dr. Nagakura (Tokyo University), who kindly gave us the opportunity of reading his manuscript in advance of publication.

* Here, a simple relation $e=\frac{\mu_{C-O}}{r}$ (e: formal charge, μ_{C-O}: the bond moment of C—O: r: the atomic distance between C and O atoms) is applied, assuming that the μ_{C-O} of *Hq* and *Q* is equal to that of aliphatic compound ($\mu_{C-O}=0.8$ D). But, as

Table 6

Calculated molecular orbitals of hydroquinone (D_{2h})



Symmetry character	Energy	Normalized M. O.
b_{3g}	$\alpha-1.987\ \beta$	0.4013 (I − IV) − 0.0916 (O − O′) − 0.4066 (II − III − V + VI)
b_{1u}	$\alpha-1.028\ \beta$	0.5550 (I + IV) − 0.2057 (O + O′) − 0.2737 (II + III + V + VI)
a_{1u}	$\alpha-\beta$	0.5000 (II − III + V − VI)
b_{3g}	$\alpha+0.285\ \beta$	0.2408 (I − IV) − 0.6100 (O − O′) + 0.1873 (II − III − V + VI)
b_{1u}	$\alpha+0.573\ \beta$	0.0729 (I + IV) + 0.6605 (O + O′) − 0.1709 (II + III + V + VI)
b_{2g}	$\alpha+\beta$	0.5000 (II + III − V − VI)
b_{3g}	$\alpha+1.382\ \beta$	0.5300 (I − IV) + 0.3465 (O − O′) + 0.2225 (II − III − V + VI)
b_{1u}	$\alpha+2.134\ \beta$	0.4322 (I + IV) + 0.1517 (O + O′) + 0.3811 (II + III + V + VI)

Table 7

Calculated π-electron densities and charge distributions of hydroquinone and quinone molecule

			O	I	II
Hq	electron density		1.902	1.062	1.018
	charge distribution	π	0.098	−0.062	−0.018
		σ	−0.118	+0.118	—
		total	−0.020	+0.056	−0.018
Q	charge distribution	π	−0.48	+0.34	+0.07
		σ	−0.14	+0.14	—
		total	−0.62	+0.48	+0.07

given in Table 6 and 7. As is shown in Table 7, the charge distributions of the π-electrons are in agreement qualitatively with Murakami's theory. However, if we take into consideration further the resultant contributions of σ-electrons of C—O* bond, the signs of the charge densities remains unchanged in the case of *Q*, while those of *Hq* change their signs and become nearly uniform. Moreover, it should be noticed that, as already shown in Fig. 3, the oxygen atoms of *Hq* actually do not lie just upon the oxygen atoms of *Q*, but rather upon the centers of benzene nuclei in the crystalline *QH*. Such a relative arrangement of component molecules is also known in the case of molecular compound between *s*-trinitrobenzene and *p*-iodoaniline[19] in the crystalline state. These two facts, i.e. the closer approach of the polarizing dipole of one component molecule to the polarizable benzene nucleus of the other, and the nearly uniform distribution of electronic charges of *Hq* molecule, will imply that the interaction energy due to the Murakami theory seems to be not so predominant. And such a relative arrangement of component molecules suggests the important role of induction effect as pointed out by Briegleb[20]. However, more precisely, each component molecule is situated in a quadrupole field resulting from the antiparallel dipole pairs of the upper and lower molecules of the other component, so that the situation is more complicated than the simple case of Briegleb.

Finally, the theory proposed recently by Mulliken[21] seems to be very significant for the explanation of the interaction energy as well as the color effect of molecular compounds in general. For the confirmation of this theory, however, thermal investigation is not sufficient and there will be necessary presumably electrical, photoelectrical, spectroscopic studies, etc.

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the degrees of hybridization of the AOs of carbon atoms in aliphatic single bonds and of aromatic σ-bonds is different, this assumption is not so exact.

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