2.86 Å. There does appear to be a valence change in Te involved in the transition.

The transition from C6 to C2 type is not a simple one. Examination of the structures leads one to the conclusion that the transition probably involves a displacement in the (11·1) planes as well as motion perpendicular to these planes. The transition also involves an appreciable contraction. The phase with the higher density (C2) is the one which is superconducting at 1.51°K.

The C6-type $RhTe_2$ appears in metallically lustrous plates with the trigonal axis perpendicular to the plate.

It is known that a substance must be a metal at room temperature in order to be a superconductor at a lower temperature. It has also been shown that a decrease in volume tends to decrease the superconducting transition temperature particularly in the case of elements (see D. Shoenberg[11]). Measurements of resistivity of the C6 type $RhTe_2$ (containing an excess of Te) were made by Dr. T. H. Geballe who found a value of 0.0035 ohm-cm. at room temperature 0.0030 ohm-cm. at 78°K. and 0.0015–0.0020 ohm-cm. at 20°K., indicating that this phase is either metallic or a degenerate semiconductor.

Hardy and Hulm[12] have reported the only case in which two intermetallic phases with the same composition are both superconducting. These are the thorium silicides $(ThSi)_2$. However, no crystallographic data are as yet available on one of these phases.

Acknowledgments.—The author wishes to thank Dr. B. T. Matthias for initiating this problem, Dr. T. H. Geballe for making the resistivity measurements, Dr. H. W. Lewis for helpful discussions. The excellent work performed by Mr. R. Goldstein in measuring the powder photographs and calculating the intensities and by Mr. E. Corenzwit in taking the powder photographs is gratefully acknowledged.

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[11] D. Shoenberg, "Superconductivity," Cambridge University Press, London, 1952.

[12] G. F. Hardy and J. K. Hulm, *Phys. Rev.*, **93**, 1004 (1954).

MURRAY HILL, N. J.

NOTES

On the Binding Energies of Some Molecular Compounds between *p*-Benzoquinone and Various Aromatic Substances

BY AKIRA KUBOYAMA[1] AND SABURO NAGAKURA

RECEIVED DECEMBER 20, 1954

In order to investigate the mechanism of the molecular compound, measurements of binding energies and characteristic absorption spectra seem to be very important.[2] Then we have measured spectrophotometrically these two quantities with molecular compounds between *p*-benzoquinone (electron acceptor by the Mulliken's definition[3]) and various aromatic substances (electron donor), such as phenol, anisole, hydroquinone, hydroquinone dimethyl ether, benzene, toluene, *o*-, *p*-xylene, naphthalene, phenanthrene and anthracene. These measurements are made with ternary solutions containing small amounts of electron acceptor and donor in a solvent. The results are given in Tables I and II. In Table I, values of the corresponding binding energy obtained by other authors, if any exist, are also shown for the purpose of comparison.

TABLE I

THE BINDING ENERGIES ($-\Delta H$) OF VARIOUS QUINHYDRONE TYPE MOLECULAR COMPOUNDS

Electron donor	Solvent	$-\Delta H$ (kcal./mole)	$-\Delta H'^{a}$ (kcal./mole)
Hydroquinone	Water (0.06 mole HCl)	2.9 ± 0.1	2.4 ± 0.4[b]
Hydroquinone	Water (0.05 mole HCl)		5.2 ± .4[c]
Dimethyl ether	*n*-Heptane	1.8 ± .1	3.5 ± .7[c]
Dimethyl ether	Carbon tetrachloride	2.1 ± .2	
Phenol	*n*-Heptane	6.6 ± .4	4.8 ± .3[c]
Phenol	Water (0.06 mole HCl)	1.2 ± .2	
Phenol	Carbon tetrachloride	4.3 ± .2	
Anisole	*n*-Heptane	1.3 ± .1	
Anisole	Carbon tetrachloride	1.2 ± .1	

[a] $-\Delta H'$ denotes the values obtained by other authors. [b] A. Berthold and S. Kunz, *Helv. Chim. Acta*, 21, 17 (1938). This value was obtained by the solubility measurement. [c] H. Tsubomura, *Bull. Chim. Soc. Japan*, 26, 304 (1953). These values were obtained by the spectroscopic method.

TABLE II

THE BINDING ENERGIES AND THE POSITIONS OF THE CHARACTERISTIC ABSORPTION BANDS OF MOLECULAR COMPOUNDS BETWEEN SEVERAL AROMATIC HYDROCARBONS AND *p*-BENZOQUINONE

Electron donor	Solvent	$-\Delta H$ (kcal./mole)	λ (mμ)	I.P. (e.v.)
Benzene	*n*-Heptane	1.8 ± 0.4	305(20°)	9.24[a]
Toluene	*n*-Heptane	1.8 ± .3	315(20°)	8.82[b]
o-Xylene	*n*-Heptane	1.8 ± .4	322(20°)	8.58[b]
p-Xylene	*n*-Heptane	1.7 ± .3	320(15°)	8.48[b]
Naphthalene	*n*-Heptane	1.5 ± .3	360(15°)	8.1[b]
Naphthalene	Carbon tetrachloride	1.4 ± .3	373(15°)	
Phenanthrene	Carbon tetrachloride	1.8 ± .4	380(15°)	
Anthracene	Carbon tetrachloride		450(7°)	

[a] W. C. Price and R. W. Wood, *J. Chem. Phys.*, **3**, 439 (1935). [b] V. G. Hammond, W. C. Price, J. P. Teegan and A. D. Walsh, *Discs. Faraday Soc.*, **9**, 53 (1950).

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[2] Until now, many spectrophotometric investigations have been made with organic molecular compounds involving *p*-benzoquinone and its derivatives as electron acceptor: L. Michaelis and S. Granick, THIS JOURNAL, **66**, 1023 (1944); H. Tsubomura, *Bull. Chem. Soc. Japan*, **26**, 304 (1953); G. Briegleb and J. Czekalla, *Z. Elektrochem.*, **58**, 249 (1954).

[3] R. S. Mulliken, THIS JOURNAL, **74**, 811 (1952); *J. Phys. Chem.*, **56**, 801 (1952).

At first some considerations will be made about the effect of solvent on the binding energy. In the molecular compound involving phenol as electron donor, its value decreases remarkably in the following order of the solvent: *n*-heptane > carbon tetrachloride > water. The similar tendency may also be expected to be observed with the molecular compound between hydroquinone and *p*-benzoquinone, but in this case it is difficult to determine the binding energy in *n*-heptane and in carbon tetrachloride because the solubility of hydroquinone in them is too small. On the other hand, in molecular compounds involving anisole and hydroquinone dimethyl ether, where the hydroxyl group of phenol and hydroquinone is replaced by the methoxyl one, the binding energy in *n*-heptane is not so different from that in carbon tetrachloride. These facts seem to suggest that there should be a special interaction between the O–H group and carbon tetrachloride. This interaction may probably be a weak hydrogen bond such as O–H---Cl.[4]

Furthermore, the results given in Tables I and II present some interesting facts as to the relationship between the binding energy and the molecular structure of the electron donor. First, it is to be noticed that the electron donating ability of the molecule containing the hydroxyl group (phenol and hydroquinone) is larger than that of the molecule containing the methoxyl one (anisole and hydroquinone dimethyl ether). One of the principal reasons for this may be that the latter group generally gives a larger steric influence than the former. Second, it is observed that in the case of *p*-disubstituted benzene as the electron donor, the binding energy is generally larger than in the case of corresponding monosubstituted one. This fact seems to be very reasonable because all forces presented until now as the cause for the molecular compound formation, such as the electrostatic, dispersion, and charge transfer forces, may be expected to become larger in the case of the former molecule.

As mentioned above, in molecular compounds involving phenol, and other similar molecules as electron donor, the binding energy changes conspicuously with the kind and number of the substituent. On the other hand, in the case of the aromatic hydrocarbon, such as benzene, naphthalene, etc., it may be regarded as almost constant, in spite of diversity of its molecular dimension and shape. At a glance, this seems to be surprising, because it may be expected that all forces mentioned above become larger in rough approximation with the dimension of the electron donor molecule. But, deeper consideration leads us to the conclusion that the charge transfer force may decrease with its increment. The reason for this is that the overlapping between electron clouds belonging to the highest occupied and the lowest vacant orbital of electron donor and acceptor, respectively, decreases as the molecular dimension of the former molecule becomes large, as is easily understood by taking the normalizing condition of the orbital wave function into consideration. Therefore, giving attention to the contribution of the charge transfer force presented by Mulliken,[3] the above-mentioned experimental result seems to be explained qualitatively without contradiction.

The positions ($\lambda_{\max}$) of the characteristic absorption for molecular compounds containing aromatic hydrocarbons as electron donor can be determined by the method described below (in the experimental part), as shown in Table II. $\lambda_{\max}$ of the molecular compound between benzene and *p*-benzoquinone in chloroform solution was already determined as 315 mμ by Andrews and Keefer.[5] This value is larger than the present one. The discrepancy between them seems to be principally due to the effect of the solvent. Inspection of this table shows that the characteristic absorptions generally shift to the longer wave length side as the ionization potential value of the electron donor becomes smaller. The similar tendency was already found by McConnell, *et al.*,[6,7] with various molecular compounds involving iodine as the electron acceptor. They explained it on the basis of the intermolecular charge transfer absorption mechanism presented by Mulliken.[3] In the present paper, it is explained by use of the molecular energy level diagram method[8] which was shown by one of the authors to be useful for the interpretation of the intramolecular charge transfer absorption observed with some unsaturated compounds containing carbonyl or nitro groups.[8] According to our method, the transition energy (ΔE) corresponding to the intermolecular charge transfer absorption can be represented by the equation

$$\Delta E = \sqrt{(I_d + V_a)^2 + 4\beta^2}$$

where I_d, V_a and β are the ionization potential (positive value) of the electron donor, the energy (negative value) of the lowest vacant level of the electron acceptor (*p*-benzoquinone) and the exchange integral between two orbitals of the problem (the highest occupied and the lowest vacant orbital of electron donor and acceptor, respectively). The above equation shows that in the first approximation, the value of ΔE should increase with the ionization potential of the electron donor, in accordance with the experimental result given in Table II.

Experimental

Materials.—*p*-Benzoquinone was purified by repeating sublimation, m.p. 114.5°. Hydroquinone was recrystallized several times from the mixture of alcohol and benzene, m.p. 172°. Hydroquinone dimethyl ether was recrystallized from alcohol, m.p. 56°. Phenol and anisole were purified repeating the vacuum distillation. Naphthalene was recrystallized several times from alcohol, m.p. 80.4–81.0°. Phenanthrene and anthracene (Merck's special grade) were used without further purification. Benzene, toluene, *n*-heptane and carbon tetrachloride were purified by the method described in "Organic Solvents."[9] *o*- and *p*-xylene were kindly supplied from Dr. Kuratani. Their purities were certified by the infrared absorption measurements.

Method.—The method for determining the binding energy is based on the Hildebrand–Benesi formula (eq. 4 in

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[4] S. Nagakura, *J. Chem. Soc. Japan*, **74**, 153 (1953).

[5] L. J. Andrews and R. M. Keefer, THIS JOURNAL, **75**, 3776 (1953).

[6] H. McConnell, J. S. Ham and J. R. Platt, *J. Chem. Phys.*, **21**, 66 (1953).

[7] S. H. Hastings, J. L. Franklin, J. C. Schiller and F. A. Matsen, THIS JOURNAL, **75**, 2900 (1953).

[8] S. Nagakura and J. Tanaka, *J. Chem. Phys.*, **22**, 236 (1954). S. Nagakura, *ibid.*, to be published.

[9] A. Weissberger and E. Proskauer, "Organic Solvents," Oxford University Press, 1935.

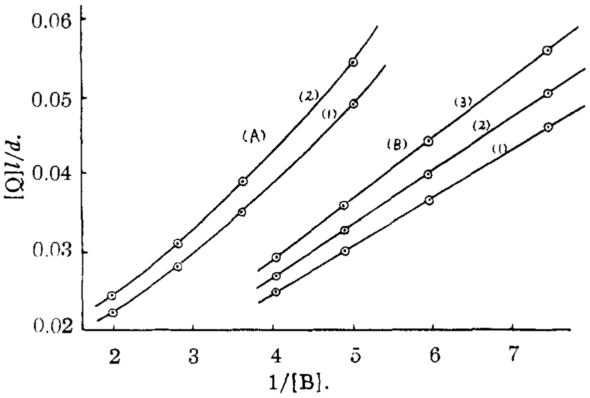

Fig. 1.—Electron donor, hydroquinone dimethyl ether: solvent, (A) carbon tetrachloride, (1) 15°, (2) 30°; (B) *n*-heptane, (1) 10°, (2) 20°, (3) 30°; wave length, 400 mμ.

their paper).[10] But it seems to be difficult to obtain the accurate value of the molar extinction coefficient (ϵ_{max}) of the absorption maximum characteristic for the molecular compound, while its product with K (equilibrium constant) can be obtained exactly from the tangent of the straight line[11] representing the relation between $[Q]l/d$ and $1/[B]$ where the meaning of each notation is the same as given in Benesi and Hildebrand's paper.[10] So we tried to obtain the binding energy by measuring the temperature dependence of $K\epsilon_{max}$. Neglecting the temperature dependence of ϵ_{max} the following equation can be derived

$$R \ln (K\epsilon_{max}) = -\Delta H/T + (\Delta S + R \ln \epsilon_{max})$$

Experimental results show that such a straight line relationship between $R \ln(K\epsilon_{max})$ and $1/T$ as expected from the above equation is satisfied in most cases (for instance see Fig. 2). Consequently, the binding energy can be obtained from its tangent. One difficulty encountered in this case is that the absorption band of the component molecule overlaps with the characteristic one of the molecular compound. In the present study, the value of extinction properly due to the latter (d in the Hildebrand–Benesi equation) was obtained by the equation

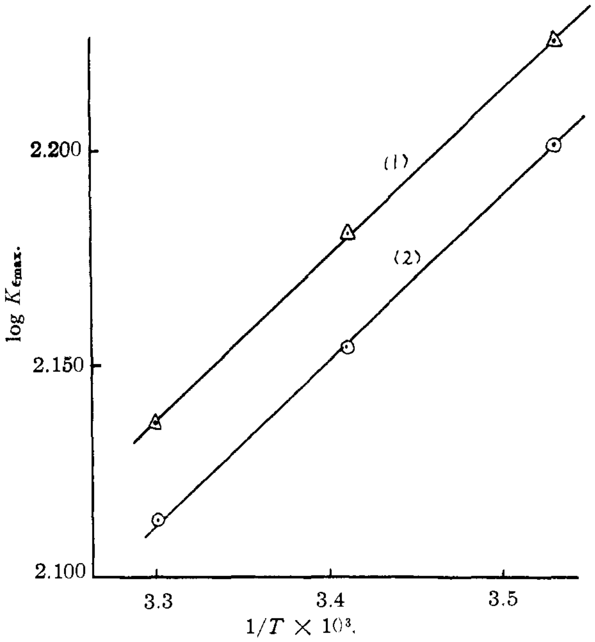

Fig. 2.—Electron donor, hydroquinone dimethyl ether; solvent, *n*-heptane; wave length (1) 413 mμ, (2) 400 mμ.

$$d = d_{obs} - d'$$

where d_{obs} and d' are the observed extinction of the solution and the sum of the extinction of all the component molecules, respectively. Since, at the wave length in question, the extinction coefficients of the absorption bands due to the component molecules are always very small, and very little portions of the component molecules added in the solution are in the binding states, the above procedure seems to be reasonable.

All the measurements of absorption spectra were made with a Beckman quartz spectrophotometer model DU. The temperature of the cell compartment was kept constant by the thermospacer during the measurement.

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[10] H. A. Benesi and J. H. Hildebrand, THIS JOURNAL, **71**, 2703 (1949).

[11] The straight line relationship between $[Q]l/d$ and $1/[B]$ was exactly satisfied in most cases (see Fig. 1) with the exception of system containing phenol, anisole and hydroquinone dimethyl ether as electron donor in carbon tetrachloride and phenol in *n*-heptane. In the latter cases, the binding energies were obtained by determining $K\epsilon_{max}$ from the values of $[Q]l/d$ measured at only two different values of [B]. The binding energy thus obtained with each molecular compound was almost constant for the various sets of [B].

Pictorial Proof of α (55°) and β' (64°) M.P. Levels for Tristearin

BY E. S. LUTTON

RECEIVED AUGUST 23, 1954

Twenty years ago Clarkson and Malkin[1] elucidated the general character of triglyceride polymorphism and showed the power of X-ray diffraction in dealing with the problem. But Malkin firmly adheres[2] to details of his position which others have criticized independently after re-examining tristearin, in particular, also with the help of X-rays.[3–5] The principal points of difference are indicated in Table I.

TABLE I

COMPARISON OF DESCRIPTIONS OF TRISTEARIN POLYMORPHISM

	B, L, F[a]			M		
Melting level	Name	Approx. m.p., °C.	Approx. L.S. (Å.)	Name	Approx. m.p., °C.	Approx L.S.. (Å.)
Lowest	α	55	50.5	Vitreous	55	None
Intermediate	β'	64	47	α	64	50.5
				β'	70	47
Highest	β	73	45	β	73	45

[a] One laboratory did not investigate intermediate melting levels of tristearin.

All would seem to agree that the differences in viewpoint have arisen from differences in experimental technique. The original difficulty is thought to lie in Malkin's use of one procedure for treating X-ray samples and another for m.p. samples; the present author has commonly used the same procedure for each and has frequently submitted a given sample to both X-ray and m.p. observation.

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(1) C. E. Clarkson and T. Malkin, *J. Chem. Soc.*, 666 (1934).

(2) T. Malkin, Chapter on "Glyceride Polymorphism" in R. T. Holman, W. O. Lundberg and T. Malkin, "Progress in the Chemistry of Fats and Other Lipids," Vol. II, Academic Press, Inc., New York, N. Y., 1954.

(3) A. E. Bailey, M. E. Jefferson, F. B. Krieger and S. T. Bauer, *J. Am. Oil Chem. Soc.*, **22**, 10 (1945).

(4) E. S. Lutton, THIS JOURNAL, **67**, 524 (1945).

(5) L. J. Filer, Jr., S. S. Sidhu, B. F. Daubert and H. E. Longenecker, *ibid.*, **68**, 167 (1946).