# 84. *Substituent Effects on the Acceptor Properties of 1,4-Benzoquinone.*

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The Hammett relation is briefly discussed and is applied to the dissociation constants of the hydrides of carbon, nitrogen, and oxygen. Charge-transfer complexes of hexamethylbenzene with monosubstituted 1,4-benzoquinones in carbon tetrachloride are studied. Cyano- and nitro-benzoquinones are described. Positions of the absorptions, association constants, and heats of formation are related to σ and the bulkiness of substituents. Large extinction coefficients, oscillator strengths, and transition dipole moments occur either with small groups or with groups which permit only very weak acceptor–donor interaction. Long-wavelength absorptions of dimethylamino-, methoxy-, iodo-, and phenyl-benzoquinones are ascribed to intramolecular charge-transfer transitions and this assignment is supported by similar absorptions in the 1-X-4-nitrobenzenes. The scatter of plots of four forms of the Benesi–Hildebrand equation is related to the strength of acceptor–donor interaction.

The most successful description of effects of substituents on chemical reactivity is the Hammett equation.[1,2] This empirical relation, which is based on benzene derivatives, must be modified when marked resonance or steric interactions occur, particularly when several substituents are present in a molecule, and to apply it successfully even to naphthalene derivatives requires a supplementary examination.[3] Nevertheless, the Hammett σ value is a consistent indication of a substituent's influence on the physical and chemical properties of a compound with which it is combined. Thus the substituent effects on the dissociation constants of the hydrides of carbon, nitrogen, and oxygen follow this order as can be seen from Table 1 and Fig. 1.

A more basic approach to the study presents two problems. First, how do substituents affect the energy levels of a molecule, particularly its ionisation potential[4] and electron affinity? Secondly, how do the energy levels determine chemical reactivity? The outcome of the study must be similar to the Hammett relation, hence the σ constant can be used with advantage to compare the results.

In this Paper the effect of substituents on the generalised acid–base (acceptor–donor) properties of 1,4-benzoquinone is measured. These are ideal for the study for the following reasons (*a*). Absorption bands of the charge-transfer complexes to which they apply are dependent on the electron affinity ($E_a$) of the acceptor, which is difficult to obtain by other techniques, and on the ionisation potential of the donor ($I_d$), where the following relation has been suggested[5]

$$h\nu_{CT} = I_d - E_a + G_1 - G_0 + X_1 - X_0, \qquad (1)$$

where $h\nu_{CT}$ is the energy of the charge-transfer transition, $G_1$ and $G_0$ are the interaction energies between donor and acceptor in the dative state and in the ground state, and $(X_1 - X_0)$ is the resonance energy of interaction between the two states.

(*b*) Resonance and steric effects, which are complicating factors in the Hammett equation, can be examined in a study of the spectra of molecular complexes. Resonance interaction,

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[1] Hammett, " Physical Organic Chemistry," McGraw-Hill, London, 1940; Taft, " Steric Effects in Organic Chemistry," Wiley, New York, 1956; Taft and Lewis, *J. Amer. Chem. Soc.*, 1959, **81**, 5343; Stock and Brown, " Advances in Physical Organic Chemistry," Academic Press, London, 1963, Vol. I, p. 35.

[2] Jaffé, *Chem. Rev.*, 1953, **53**, 191; van Bekkum, Verkade, and Wepster, *Rec. Trav. chim.*, 1959, **78**, 815.

[3] Dewar and Grisdale, *J. Amer. Chem. Soc.*, 1962, **84**, 3539, 3548.

[4] Crable and Kearns, *J. Phys. Chem.*, 1962, **66**, 436.

[5] Mulliken and Person, *Ann. Rev. Phys. Chem.*, 1962, **13**, 107.

TABLE 1.

Substituent effects on the dissociation constants in water of the hydrides of carbon, nitrogen, and oxygen.

| | | Dissoc. constants (p$K_a$) | | | | | Dissoc. constants (p$K_a$) | | |
|---|---|---|---|---|---|---|---|---|---|
| Subst. | $\sigma$ | $CH_4$ | $NH_3$ | $H_2O$ | Subst. | $\sigma$ | $CH_4$ | $NH_3$ | $H_2O$ |
| $ClO_3$ ............ | — | — | 5·5 | (−10) | CN ............ | 0·63 | (18) (25) | 10·3 | 3·9 |
| $NO_2$ ............ | 0·78 | 10·2 | 6·5 | −1·4 | COMe ......... | 0·52 | 20 | 15·1 | 4·8 |
| $SO_2Me$ ......... | 0·73 | (23) | 10·8 | −0·6 | H .............. | 0·00 | (58) | (35) | 15·7 |

p$K_a$ values in parentheses are approximate. Tautomerism has not been considered. Values of the Hammett $\sigma_p$ come from Jaffé.[2] The correlation also applies to other $\sigma$ values.[1, 2] Dissociation constants come from: Pearson and Dillon, *J. Amer. Chem. Soc.*, 1953, **75**, 2439; Parsons, " Handbook of Electrochemical Constants," Butterworths, London, 1959; Kameyama, *Trans. Electrochem. Soc.*, 1921, **40**, 134; Branch and Clayton, *J. Amer. Chem. Soc.*, 1928, **50**, 1680; Junell, *Z. phys. Chem.* (*Leipzig*), 1929, **141**, 71; Bonhoeffer, Geib, and Reitz, *J. Chem. Phys.*, 1939, **7**, 664; Turnbull and Maron, *J. Amer. Chem. Soc.*, 1943, **65**, 212; Bell, *Trans. Faraday Soc.*, 1943, **39**, 253; Bascombe and Bell, *J.*, 1959, 1096; Vekemans and Bruylants, *Bull. Soc. chim. belges*, 1959, **68**, 504; Mandell and Barth-Wehrenalp, *J. Inorg. Nuclear Chem.*, 1959, **12**, 90; Hinman and Hoogenboom, *J. Org. Chem.*, 1961, **26**, 3461; Bell, " The Proton in Chemistry," Methuen, London, 1959.

an indication of low lying excited states, may be associated with intramolecular charge-transfer absorption in one of the components, whereas bulky groups alter markedly the association constants of planar 1 : 1 adducts. Association constants, $K$, and extinction coefficients, $\varepsilon$, are obtained from the Benesi–Hildebrand relation

$$\alpha b/D = b/\varepsilon + 1/K\varepsilon, \tag{2}$$

where $\alpha$ is the constant acceptor concentration, $b$ the varied donor concentration ($b \gg \alpha$), $D$ the optical density for 1 cm. light path, corrected for absorption by the acceptor and usually taken at maximum extinction.

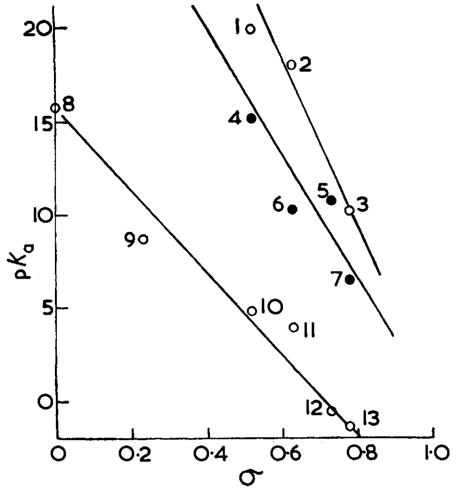

FIG. 1. Dissociation constants of the hydrides of carbon, nitrogen, and oxygen. 1, MeCOMe; 2, MeCN; 3, $MeNO_2$. 4, $NH_2$·COMe; 5, $NH_2$·$SO_2$Me; 6, $NH_2$·CN; 7, $NH_2$·$NO_2$. 8, HOH; 9, HOBr; 10, HO·COMe; 11, HO·CN; 12, HO·$SO_2$Me; 13, HO·$NO_2$.

The lines are:

$$pK_a(H_2O) = -22{\cdot}1\sigma + 15{\cdot}7$$
$$pK_a(NH_3) = -35{\cdot}4\sigma + 35$$
$$pK_a(CH_4) = -51{\cdot}6\sigma + 52$$

(*c*) Moreover, strong acceptors and strong donors are generally very reactive compounds. 1,4-Benzoquinone is a quite strong organic $\pi$-electron acceptor,[6] being comparable with 1,3,5-trinitrobenzene of the substituted benzene series. Despite the fact that a suitable choice of substituents is likely to enhance its strength, there has been little study of the chemistry of these compounds. Cyano- and nitro-benzoquinones have not been reported. Complexes of the monosubstituted benzoquinones of Table 2 with hexamethylbenzene in carbon tetrachloride are examined here.

[6] Chowdhury, *Trans. Faraday Soc.*, 1961, **57**, 1482; Foster, Hammick, and Placito, *J.*, 1956, 3881.

Studies related to the present one are as follows. The effect of substituents on the equilibrium constants of anthracene with trinitrobenzenes and of anilines with trinitrobenzene was not in the order of the $\sigma$ constant.[7] Preliminary reports have appeared on the charge-transfer bands of complexes of aniline with tetrachlorobenzoquinone and of anisoles with tetracyanoethylene,[8] whereas the charge-transfer bands of a few 1-X-benzyl-4-methoxycarbonylpyridinium iodides [9] follow the $\sigma$ constant. Substituents affect the intramolecular charge-transfer bands of phenylazoazulenes,[10] and silver complexes of benzene derivatives have been studied by a partition method.[11]

## EXPERIMENTAL

Details of the instrument and of the purification of solvent and hexamethylbenzene have been given previously.[12] In this experiment one cm. cells were used. With the exception of iodo-, phenyl-, methoxy-, and dimethylamino-benzoquinone, acceptor absorptions at the positions of the charge-transfer bands were small. Identical acceptor concentrations were used in the instrument's compensating beam for all measurements, hence it was necessary to have low concentrations of phenyl-, methoxy-, and dimethylamino-benzoquinone, to prevent large changes in the automatic slit of the Cary spectrophotometer.

*Preparation of Benzoquinones.—Benzoquinone.* Two crystallisations from ethanol, followed by sublimation at 0·1 mm. at room temperature, produced yellow crystals, m. p. 112·5—113·5°. *Dimethylaminobenzoquinone. m*-Dimethylaminophenol, crystallised from light petroleum, was oxidised by Fremy's salt [13] to the benzoquinone,[14] which was crystallised five times from ether at −80°. The deep purple crystals had m. p. 108—109° (Found: C, 63·8; H, 6·3; N, 9·2, 9·2. Calc. for $C_8H_9NO_2$: C, 63·5; H, 6·0; N, 9·3%).

*Methoxybenzoquinone.* A sample that had darkened during several years storage was crystallised twice from methanol to give golden needles, m. p. 144—145°. *Methylbenzoquinone.* This, crystallised twice from ethanol, had m. p. 68—69°.

*Phenylbenzoquinone.* The method of Brassard and l'Écuyer [15] gave golden crystals, m. p. 112·5—113·5° [from petroleum (b. p. 60—80°)] (Found: C, 78·8; H, 4·7. Calc. for $C_{12}H_8O_2$: C, 78·3; H, 4·4%). *Fluorobenzoquinone.* A cold solution of diazotised sulphanilic acid (from 10 g. of the acid) was added to *m*-fluorophenol (5·6 g.) in aqueous potassium hydroxide (6·0 g. or more if necessary to maintain alkalinity). After ½ hr. sodium dithionite (24 g.) was added. The red dye disappeared on being warmed and crystals of 4-amino-3-fluorophenol were deposited from the chilled solution, m.p. 138—139° (from water) (Found: C, 56·4; H, 4·8; N, 11·1. Calc. for $C_6H_6FNO$: C, 56·7; H, 4·7; N, 11·0%). To a stirred solution of the aminophenol (1 g.) in 25% sulphuric acid (30 ml.) at 2° was slowly added a concentrated solution of sodium dichromate (1·5 g.). The precipitated quinone was washed, dried, and sublimed (40°/0·1 mm.), giving pale yellow crystals, m. p. 80·5—81·5° (lit.,[16] 80°) (Found: C, 56·8; H, 2·7. Calc. for $C_6H_3FO_2$: C, 57·1; H, 2·4%).

*Chlorobenzoquinone.* Two crystallisations from ethanol gave yellow crystals, m. p. 57—58°.

*Bromobenzoquinone.* Bromoquinol was oxidised with silver oxide. The quinol (M/40), silver oxide (9 g.), and anhydrous sodium sulphate (9 g.) were stirred vigorously in dry ether (150 ml.) for ½ hr. The course of the reaction could be followed by spotting the liquid on filter paper, for when reaction was complete no strongly coloured ring of the quinhydrone appeared. Filtration, evaporation, and crystallisation from petroleum (b. p. 40—60°) gave orange crystals, m. p. 55—56°.

*Iodobenzoquinone.* Sublimation at 40°/0·1 mm. gave brown crystals, m. p. 63—64° (lit.,[17] 62°) (Found: C, 31·1; H, 1·4. Calc. for $C_6H_3IO_2$: C, 30·8; H, 1·3%).

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[7] Ross, Bassin, and Kuntz, *J. Amer. Chem. Soc.*, 1954, **76**, 4176.

[8] Plummer and White, " Abstracts of Papers," American Chemical Society, 1962, Vol. 142, p. 86Q.

[9] Kosower, Hofmann, and Wallenfels, *J. Amer. Chem. Soc.*, 1962, **84**, 2755.

[10] Gerson and Heilbronner, *Helv. Chim. Acta*, 1959, **42**, 1877.

[11] Andrews and Keefer, *J. Amer. Chem. Soc.*, 1950, **72**, 3113.

[12] Hammond, *J.*, 1963, 3113.

[13] Palmer, " Experimental Inorganic Chemistry," Cambridge Univ. Press, 1959, p. 281.

[14] Teuber and Hasselbach, *Chem. Ber.*, 1959, **92**, 674.

[15] Brassard and l'Écuyer, *Canad. J. Chem.*, 1958, **36**, 700.

[16] Hodgson and Nicholson, *J.*, 1941, 645.

[17] Kvalnes, *J. Amer. Chem. Soc.*, 1934, **56**, 667.

*Methoxycarbonylbenzoquinone.* Oxidation of gentisic acid methyl ester with silver oxide, as used for the oxidation of bromoquinol, did not go to completion. Sublimation (60°/0·1 mm.) of the brown residue gave brown crystals, which crystallised from carbon disulphide to give a mixture of orange prisms and fine red needles. The latter, presumably the quinhydrone, m. p. 85°, could be removed by sliding the material along filter paper, when the needles adhered to the fibres of the paper. Repeating the process five times gave orange crystals, visibly free from impurities, m. p. 53·8—54·8° (from pure carbon disulphide) (lit.,[18] 54°) (Found: C, 57·2; H, 3·3. Calc. for $C_8H_6O_4$: C, 57·8; H, 3·6%)

*Acetylbenzoquinone.* Sublimation of the benzoquinone (60°/0·1 mm.) gave orange crystals, m. p. 65—66° (lit.,[19] 65·5—66·5°), which darkened during two months over calcium chloride, in the absence of light.

*Attempted preparation of methyl 2,5-dihydroxybenzenesulphonate.* The major product identified from refluxing quinol in dimethyl sulphate was *p*-hydroxyanisole. A small amount of material, which in ether exhibited a strong blue fluorescence and which stabilised ether–water emulsions, was also present.

*Cyanobenzoquinone.* The Elbs oxidation of *o*-cyanophenol [20] produced a deep brown solution. Carbon dioxide was bubbled through the mixture for 2 hr., surplus *o*-cyanophenol extracted into ether, and the aqueous layer warmed with an excess of concentrated hydrochloric acid. Shaking the liquid with ether gave a persistent emulsion which could be broken up only by adding salt and centrifuging. A brown, amorphous solid which could not be crystallised from the common solvents was obtained by drying and evaporating the ether extracts, and small, analytically pure samples of cyanoquinol, prepared by sublimation at 120°/0·1 mm., had m. p. 165—167° (lit.,[20] 165—167°) (Found: C, 62·6; H, 3·7; N, 10·5. Calc. for $C_7H_5NO_2$: C, 62·2; H, 3·7; N, 10·4%). No reaction of this with silver oxide was observed, although oxidation with nitrogen oxides produced the benzoquinone from both the pure and crude materials. Nitrogen oxides [12] (1 ml.) were added to a stirred suspension of the quinol (3 g.) in carbon tetrachloride (50 ml.) at −10°. The liquid was filtered after 10 min., fresh carbon tetrachloride (150 ml.) was added to the filtrate, and the brown precipitate was washed with chloroform (20 ml.). This left a brown gum on the filter and produced a suspension of crystals in the filtrate. Two crystallisations of the latter from fresh carbon tetrachloride gave *cyanobenzoquinone* * as stable, golden-brown crystals, m. p. 121—122° (Found: C, 62·6; H, 2·3; N, 10·9. $C_7H_3NO_2$ requires C, 63·2; H, 2·3; N, 10·5%). Mixtures of the benzoquinone with solutions of amines and aromatic hydrocarbons were coloured. With hexamethylbenzene for example they were red.

*Nitrobenzoquinone.* Silver oxide could not be made to oxidise nitroquinol,[21] and nitrogen oxides had to be used. To the quinol (3 g.) and Molecular Sieve type 4A (10 g.) in stirred dichloromethane (50 ml.), cooled in an acetone–ice bath, were added nitrogen oxides (1·5 ml.). After 15 min. the suspension was filtered through a sintered glass funnel and the green solution was evaporated to half its volume at room temperature. Carbon tetrachloride (150 ml.) was added and this was evaporated to half volume at room temperature. The flask at this stage contained a suspension of yellow, crystalline plates, which could be stored in a desiccator over sulphuric acid, potassium hydroxide, and wax at 1 mm. Part of the solution was diluted with carbon tetrachloride and used directly in the spectrophotometric studies.

The crystals gave intense colours with amines and aromatic hydrocarbon solutions, red-violet with hexamethylbenzene and blue with dimethylaniline. Nujol mulls showed no OH vibration frequencies. The colour of carbon tetrachloride solutions containing hexamethylbenzene could be ascribed to the formation of a charge-transfer complex, since a single, broad, structureless band was observed immediately the mixture was prepared, which was not possessed by either component separately. Beer's law was not obeyed, although the Benesi–Hildebrand relation for colour intensity was. Moreover the spectra were due to a stronger acceptor than the monosubstituted benzoquinones 2—13 in Table 2. The position of maximum absorption

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* This compound has now been prepared by Ansell, Nash, and Wilson (*J.*, 1963, 3028) and by Professor Wallenfels (private communication). The reported physical properties are in close agreement.

[18] Brunner, *Monatsh.*, 1903, **34**, 916.

[19] Kloetzel, Dayton, and Abadir, *J. Org. Chem.*, 1955, **20**, 38.

[20] Seebeck, *Helv. Chim. Acta*, 1947, **30**, 149.

[21] Elbs, *J. prakt. Chem.*, 1893, **48**, 179.

(535 mμ), and the strength of the association (5·51 l. mole$^{-1}$), could reasonably be predicted for *nitrobenzoquinone* from the trend in values for the other benzoquinones.

Nitrobenzoquinone, m. p. about 45° (decomp.) (not reproducible), in air decomposed to a brown gum within 1 hr. and brown nitrogen oxides were seen over the crystals in a dry sample tube within 10 min. The compound lost its ability to form coloured complexes with aromatic hydrocarbons when it was stored in a desiccator for 6 days. Solutions in dichloromethane lost their colour-forming property after 3 days and a brown gum was simultaneously deposited on the walls of the flask. Nujol mulls of the gum exposed to air showed OH vibration frequencies at 3300 cm.$^{-1}$. Because of this instability, measurements of $\Delta H$ and $\varepsilon$ were not attempted. The compound could be crystallised from warm carbon tetrachloride and it dissolved in water during 10 min. giving a red-brown, strongly acid solution.

## RESULTS

Single, broad, structureless bands, which were not present in the spectra of either component separately, were observed immediately the benzoquinones were mixed with hexamethylbenzene. Apart from the absorptions shown in Table 2, no other changes in spectra occurred.

TABLE 2.

Complexes of monosubstituted 1,4-benzoquinones with hexamethylbenzene in carbon tetrachloride at 25°.

| Benzoquinone | $K$ (l. mole$^{-1}$) | $-\Delta$H (kcal. mole$^{-1}$) | $\nu_{\text{CT}}$ mμ | ev | $\Delta\nu_{\frac{1}{2}}$ ev | $10^{-3}\varepsilon_{\text{max.}}$ | $10^2 f$ | μ (D) |
|---|---|---|---|---|---|---|---|---|
| 1. Nitro ………………… | 5·51 | — | 535 | 2·32 | 0·82 | — | — | — |
| 2. Cyano ………………… | 4·11 | 5·8 | 487 | 2·55 | 0·67 | 2·67 | 6·2 | 2·5 |
| 3. Acetyl ………………… | 1·21 | 4·5 | 454 | 2·73 | 0·67 | 1·53 | 3·6 | 1·9 |
| 4. Methoxycarbonyl… | 0·72 | 3·7 | 446 | 2·78 | 0·74 | 2·29 | 5·9 | 2·4 |
| 5. Fluoro ………………… | 0·85 | 4·2 | 433 | 2·86 | 0·68 | 2·57 | 6·1 | 2·4 |
| 6. Chloro ………………… | 1·20 | 4·5 | 442 | 2·80 | 0·72 | 1·93 | 4·9 | 2·1 |
| 7. Bromo ………………… | 2·11 | 5·6 | 444 | 2·79 | 0·74 | 1·07 | 2·8 | 1·6 |
| 8. Iodo ………………… | 1·95 | 4·5 | 439 | 2·82 | 0·66 | 1·11 | 2·6 | 1·5 |
| 9. Phenyl ………………… | ~0·10 | 3·5 | 428 | 2·90 | 0·59 | ~5·5 | ~11·3 | ~3·2 |
| 10. Hydrogen ………… | 0·71 | 4·1 | 416 | 2·98 | 0·77 | 1·86 | 5·0 | 2·1 |
| 11. Methyl ………………… | 0·57 | 3·7 | 410 | 3·02 | 0·74 | 1·69 | 4·3 | 1·9 |
| 12. Methoxy ………… | 0·18 | 4·4 | 397 | 3·12 | 0·85 | 4·81 | 14·2 | 3·5 |
| 13. Dimethylamino … | ~0·10 | 2·0 | 370 | 3·35 | 0·63 | ~7·0 | ~15·3 | ~3·5 |

The Benesi–Hildebrand equation can be expressed in four ways:

$$\alpha b/D = 1/K\varepsilon + b/\varepsilon \quad \text{(3A)} \qquad b/D = 1/K\varepsilon\alpha + b/\varepsilon\alpha \quad \text{(3B)}$$

$$\alpha/D = 1/K\varepsilon b + 1/\varepsilon \quad \text{(3C)} \qquad 1/D = 1/K\varepsilon\alpha b + 1/\varepsilon\alpha, \quad \text{(3D)}$$

and from plots of $\alpha b/D$ against $b$ (for A), $b/D$ against $b$ (for B), $\alpha/D$ against $1/b$ (for C), or $1/D$ against $1/b$ (for D), $K$ and $\varepsilon$ values can be estimated from the intercepts or slopes of the graphs if straight lines are obtained. The complexes of the benzoquinones in Table 3 were examined in a similar manner, namely, acceptor concentrations were suitably chosen to give measurable optical densities (about 0·4 to 1·1) for a preselected range of donor concentrations. The figures in Table 3 are the least-squares estimates of the slopes for the four plots, together with their standard errors. Table 3 and Fig. 2 show that the equations (3A—D) are obeyed. A one per cent error in optical density, or acceptor or donor concentration can account for most of the experimental scatter.

Table 2 shows $K$ and $\varepsilon$ values for the complexes, calculated from the least-squares estimates of the slopes and intercepts for plots of the equation D, which from Table 3 can be seen to have the smallest fractional standard errors.

Measurements on the benzoquinones (6), (10) and (11) are in close agreement with those previously reported.[6] $K$ and $\varepsilon$ for phenyl-, methoxy-, and dimethylamino-benzoquinone

TABLE 3.

Gradients and standard errors by a least-squares treatment of the experimental information for four plots of the Benesi–Hildebrand relation.

| Benzoquinone | Plot A<br>$10^3/\varepsilon$ | Plot B<br>$1/\varepsilon\alpha$ | Plot C<br>$10^3/K\varepsilon$ | Plot D<br>$1/K\varepsilon\alpha$ |
|---|---|---|---|---|
| 1. Nitro | — | 0·514 ± 0·006 | — | 0·0962 ± 0·0009 |
| 2. Cyano | 0·370 ± 0·006 | 0·460 ± 0·005 | 0·0910 ± 0·0006 | 0·1128 ± 0·0005 |
| 3. Acetyl | 0·55 ± 0·07 | 0·16 ± 0·02 | 0·539 ± 0·007 | 0·153 ± 0·002 |
| 4. Methoxycarbonyl | 0·48 ± 0·04 | 0·134 ± 0·011 | 0·607 ± 0·003 | 0·1704 ± 0·0007 |
| 5. Fluoro | 0·39 ± 0·02 | 0·167 ± 0·008 | 0·456 ± 0·002 | 0·1970 ± 0·0006 |
| 6. Chloro | 0·54 ± 0·07 | 0·22 ± 0·02 | 0·436 ± 0·006 | 0·171 ± 0·002 |
| 7. Bromo | 0·77 ± 0·10 | 0·30 ± 0·04 | 0·443 ± 0·013 | 0·168 ± 0·005 |
| 8. Iodo | 0·83 ± 0·11 | 0·27 ± 0·04 | 0·454 ± 0·012 | 0·151 ± 0·005 |
| 10. Hydrogen | 0·58 ± 0·06 | 0·17 ± 0·02 | 0·763 ± 0·006 | 0·217 ± 0·002 |
| 11. Methyl | 0·54 ± 0·09 | 0·13± 0·03 | 1·030 ± 0·010 | 0·269 ± 0·004 |

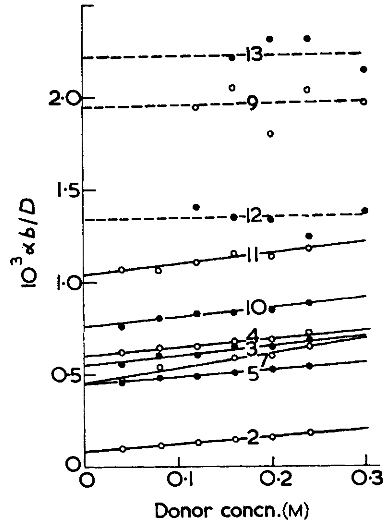

FIG. 2. Plot A of the Benesi–Hildebrand relation for complexes of monosubstituted benzoquinones with hexamethylbenzene.

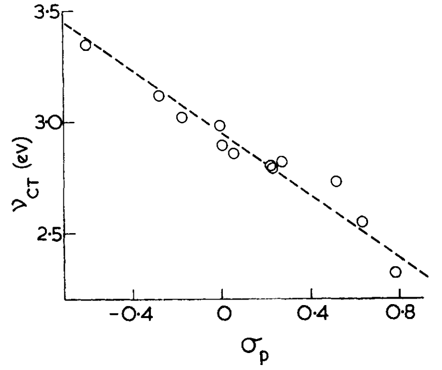

FIG. 3. Energy of the charge-transfer absorption for the complexes listed in Table 2.

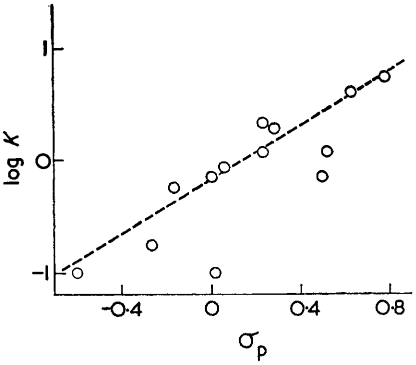

FIG. 4. Equilibrium constants for the complexes listed in Table 2.

were found by graphical extrapolation and optical-density measurements for these were subject to large experimental error. The enthalpies of formation ($\Delta H$) of the complexes were obtained from the formula

$$\Delta H = [2{\cdot}303\mathbf{R}T_1T_2/(T_2 - T_1)] \log [(\alpha\varepsilon/D_1 - 1)/(\alpha\varepsilon/D_2 - 1)] \qquad (4)$$

where $\boldsymbol{R}$ is the gas constant and $T_1$ and $T_2$ are the temperatures (298°K and 323°K) at which the optical densities $D_1$ and $D_2$ were measured for a particular acceptor–donor pair. The assumptions used in the estimation, namely that $\varepsilon$ and $\Delta H$ do not vary over the temperature range, are approximate, particularly for small values of $K$.[22]

Oscillator strengths $f$ and transition dipole moments $\mu$ were calculated from formulæ [5,23] that involved $\Delta\nu_{\frac{1}{2}}$, the width of the bands at half intensity.

Figs. 3 and 4 show plots of the energies of the charge-transfer absorptions and of the logarithms of the equilibrium constants against the Hammett $\sigma_p$.

## DISCUSSION

The main conclusion of this study is that substituents enhance the acceptor properties of the $\pi$-electron system of 1,4-benzoquinone towards hexamethylbenzene, in the order of the Hammett $\sigma_p$ constant. In particular, positions of maximum absorption for the charge-transfer bands follow the constant closely. That Fig. 3 shows a nearly linear plot is certainly accidental, particularly as values of $\sigma_p$ for $+M$ groups are inconsistent.[2] On the other hand, some justification for preferring this constant to the more precise one of Bekkum, Verkade, and Wepster [2] comes from the similarity of benzoquinone to benzene carrying $-M$ substituents, and values of $\sigma$ are based on the $-M$ carboxyl group. Association constants and enthalpies of formation are also in this order, except that firmer complexes occur with small substituents (CN, F, H) and weaker complexes occur with bulky substituents (COMe, $CO_2Me$,Ph). This is as expected for the formation of parallel plane-to-plane adducts. The restricted number of compounds examined probably accounts for the absence of such a correlation [7] in the acceptor properties of trinitrobenzenes and the donor properties of anilines.

If the stability of the complexes arises from resonance interaction of dative and no-bond structures [24] or from mutual perturbation of donor and acceptor orbitals [25] then the transition energies are obtained from

$$\boldsymbol{h}\nu_{CT} = I_d - E_a + \text{Constant} \qquad (5)$$

Provided very firm complexes [12,26] are not included, and they are not in this study, the equation is obeyed approximately [27] for many donor–acceptor pairs, particularly for comparisons of similar molecules. Thus changes of positions of the bands with hexamethylbenzene may be equivalent to changes of electron affinities of the benzoquinones. The values of $K$ show that other factors contribute to the interaction, and hence a refinement of eqn. (5), such as eqn. (1), should strictly be applied. An independent measurement related to electron affinity is the polarographic reduction potential.[28] The close correspondence of the half-wave potentials in acetonitrile [29] of the benzoquinones (6), (9), (10), and (11) with the energies of the transitions in column 4 of Table 2 support the view that the values in this column directly reflect changes in electron affinities. Theoretical estimates [30] of the energy of the lowest unoccupied orbital of benzoquinone are not in

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[22] Orgel and Mulliken, *J. Amer. Chem. Soc.*, 1957, **79**, 4839; Mulliken, *Rec. Trav. chim.*, 1956, **75**, 845; Murrell, *J. Amer. Chem. Soc.*, 1959, **81**, 5037.

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[25] Dewar and Lepley, *J. Amer. Chem. Soc.*, 1961, **83**, 4560.

[26] Merrifield and Phillips, *J. Amer. Chem. Soc.*, 1958, **80**, 2778; Melby, Harder, Hertler, Mahler, Benson, and Mochel, *J. Amer. Chem. Soc.*, 1962, **84**, 3374; Yada, Tanaka, and Nagakura, *Bull. Chem. Soc. Japan*, 1960, **33**, 1660.

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[28] Maccoll, *Nature*, 1949, **163**, 178; Pullman, Pullman, and Berthier, *Bull. Soc. chim. France*, 1950, **17**, 591; Peover, *Nature*, 1961, **191**, 702; 1962, **193**, 475.

[29] Peover, *J.*, 1962, 4540.

[30] Orgel, *Trans. Faraday Soc.*, 1956, **52**, 1172; Pullman, *Compt. rend.*, 1961, **253**, 1210; Nagakura and Kuboyama, *J. Chem. Soc. Japan*, 1953, **74**, 499; Kuboyama, *Bull. Chem. Soc., Japan*, 1958, **31**, 752.

forms that permit a direct evaluation of electron affinity. Neither are measurements of this quantity [27,31] (0·77, 1·46—0·76, and 2·02 ev) in sufficient agreement to enable a table of absolute values to be compiled.

Small substituents (CN, F, H) are associated with large extinction coefficients, oscillator strengths, and transition dipole moments in the complexes, indicating that the degree to which the transition is allowed increases when the components can approach one another closely. Values of $\varepsilon$, $f$, and $\mu$ are also large for the benzoquinones (9), (12), and (13). Plots of the Benesi–Hildebrand equation in the forms (3C) or (3D) are the most suitable for displaying this since the gradients are $1/K\varepsilon$ and $1/K\varepsilon\alpha$, respectively. As $K$ decreases, the slopes increase markedly (by a factor of ten as $K$ varies between 1·0 and 0·1) if there are no changes in $\varepsilon$ or $\alpha$. Although the slopes were steeper for small values of $K$, they did not alter to this extent and they could be accommodated only by increases in $\varepsilon$ as shown in Table 2. An explanation for changes in $\varepsilon$ and $f$ is that contact charge-transfer absorption [22] contributes a major part of the bands in the weaker complexes ($K < 0{\cdot}5$), whereas transitions between parallel 1 : 1 pairs in solution account for most of the intensity of the firmer.

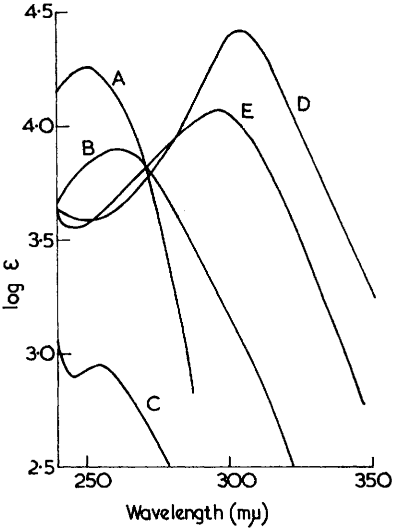

FIG. 5. Light absorptions in ethanol.

A, Biphenyl.
B, Nitrobenzene.
C, Iodobenzene.
D, 4-Nitrobiphenyl.
E, *p*-Iodonitrobenzene.

With the exceptions listed below, absorptions of the benzoquinones at wavelengths greater than **300** m$\mu$ are weak. Bands at **500** m$\mu$ ($\varepsilon$ **5600**) in dimethylaminobenzoquinone and at **346** m$\mu$ ($\varepsilon$ **972**) in methoxybenzoquinone interfered with measurements on spectra of the complexes. The positions of these suggest that they are intramolecular charge-transfer absorptions involving the donor substituents and the acceptor benzoquinone nuclei. Similar transitions from the polarisable iodine atom and from the phenyl $\pi$-electrons may account for bands in iodobenzoquinone at 377 m$\mu$ ($\varepsilon$ 1250) and in phenylbenzoquinone at 369 m$\mu$ ($\varepsilon$ 2,460). On the other hand, as the value of $K$ for the complex in Table 2 implies free rotation of the phenyl group, conditions should be unfavourable for this second absorption, which obeys Beer's law. In support of the assignments it is of interest to compare the spectra of the 1-X-4-nitrobenzenes. Long-wavelength absorptions which are not present in nitrobenzene, *NN*-dimethylaniline, or anisole, appear for the dimethylamino-compound [32,33] at 390 m$\mu$ and in the methoxy-compound [34] at 305 m$\mu$. The transition dipole moment of the first lies along the longitudinal axis of the molecule.[32]

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[31] Briegleb and Czekalla, *Angew. Chem.*, 1960, **72**, 401; Batley and Lyons, *Nature*, 1962, **196**, 573.
[32] Czekalla and Wick, *Z. Elektrochem.*, 1961, **65**, 727.
[33] Kumler, *J. Amer. Chem. Soc.*, 1946, **68**, 1184.
[34] Burawoy and Chamberlain, *J.*, 1952, 3734.

Fig. 5 shows that the iodo- and phenyl-compounds also have additional long-wavelength absorptions. Replacement of the iodine atom by bromine and chlorine shifts[35] the maximum from 295 mμ to 275 mμ and 270 mμ, and in the benzoquinone shifts the maximum from 377 mμ to 332 mμ and 325 mμ. Explanations of the spectra of the 1-halogeno-4-nitrobenzenes[36] and of the halogenobenzoquinones therefore support each other.

Apart from the difference in experimental scatter for the four plots of the Benesi–Hildebrand equation, Table 3 and Fig. 2 show that the relative scatter in plots A and B is small for the strong acceptors (nitro- and cyano-benzoquinone) and is large for the weak acceptors (benzoquinone and methylbenzoquinone) even though optical densities, acceptor concentrations, and donor concentrations are measured with the same accuracy throughout. This is considered in greater detail elsewhere.[37]

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[37] Hammond, following paper.