571. *A Study of Complexes of* 1,4-*Benzoquinones, carrying Electronegative Substituents, with Some Methylbenzenes.*

By P. R. Hammond.

Colours formed in mixtures containing methylbenzenes and 2,3-dicyanobenzoquinone or 2,3-dichloro-5,6-dicyanobenzoquinone in carbon tetrachloride and dichloromethane are assigned to charge-transfer transitions. Association constants, extinction coefficients, and heats of association for the 1 : 1 complexes are reported where possible. The dicyanobenzoquinone–hexamethylbenzene and dichlorodicyanobenzoquinone–durene complex have been isolated and their constitution, melting points, and infrared and electron spin resonance spectra are briefly described together with the nuclear magnetic resonance spectra of concentrated solutions of the benzoquinones in mesitylene. Unstable 2,6-dinitrobenzoquinone has been prepared and is characterised by the charge-transfer transitions in its complexes with methylbenzenes. The measurements show that the three benzoquinones are comparable with tetracyanoethylene in acceptor strength.

Acceptor properties of the *p*-benzoquinones are well established from studies of their charge-transfer complexes with aromatic hydrocarbons.[1] Spectral investigations [1b,2] indicate that *p*-benzoquinone is an acceptor comparable in strength with 1,3,5-trinitrobenzene. Moreover, electronegative substituents attached to the organic acceptor system enhance complex formation and lower the frequency of absorption of the charge-transfer transition in a series of complexes with a particular donor.[3] These are properties typical

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[1] (*a*) Foster, Hammick, and Placito, *J.*, 1956, 3881; (*b*) Chowdhury, *Trans. Faraday Soc.*, 1961, **57**, 1482.

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

[3] Hammond, *J.*, in the press.

of strong acceptors. Hence cyano- or nitro-groups bonded to the benzoquinone nucleus should form molecules with interesting properties.

The few organic acceptors capable of making firm complexes, for example, tetracyanoethylene, chloranil, and tetracyanoquinodimethane, are chemically reactive. A study is made here, where possible, of properties including the infrared, nuclear magnetic resonance, electron spin resonance, and, particularly, the visible and ultraviolet spectra of the complexes of 2,3-dicyano-, 2,3-dichloro-5,6-dicyano-, and 2,6-dinitro-benzoquinone with some methylbenzenes. It is expected that these properties will serve as a basis for further investigations of the chemical reactivity of the benzoquinones.

EXPERIMENTAL

2,3-Dichloro-5,6-dicyanobenzoquinone, crystallised twice from benzene–chloroform (1 : 4), had m. p. 215—217°. Hexamethylbenzene (m. p. 165—165·5°) and durene (m. p. 81—82°) were crystallised twice from ethanol. " Puriss." mesitylene (Aldrich) was fractionally distilled and no impurities were detected by vapour-phase chromatography over zeolite impregnated with 10% of silicone oil. The xylenes and toluene were fractionally distilled and their purities checked by vapour-phase chromatography.

For the preparation of nitrogen oxides, five times the amount of reactants prescribed by Brook [4] were distilled and the product was condensed by an efficient triple-surface condenser combined with a trap cooled in acetone–solid carbon dioxide. The liquid separated into two layers, and the upper one distilled from a bath at 50°.

2,3-Dicyanobenzoquinone,[4] crystallised twice from a large volume of chloroform, had m. p. 182—183°.

2,6-*Dinitrobenzoquinone.*—Quinol diacetate was treated with fuming nitric acid; the resulting 4-acetoxy-2,6-dinitrophenol was hydrolysed and the quinol was oxidised with nitrogen oxides.

4-*Acetoxy*-2,6-*dinitrophenol.*—The yellow compound obtained by nitration of quinol diacetate[5] was crystallised from ethanol; it had m. p. 94—96° (Found: C, 40·4; H, 2·8; N, 11·7. Calc. for $C_8H_6N_2O_7$: C, 39·7; H, 2·5; N, 11·6%). A comparison of the infrared spectra of Nujol mulls of the acetate (A), nitroquinol (B), and dinitroquinol (C) confirmed Richter's[6] structure, since the O–H systems in (B) and (C) exhibited less hydrogen bonding than that in (A) (OH vibration frequencies 3450 and 3375 cm.$^{-1}$ compared with a weak absorption at 3220 cm.$^{-1}$).

2,6-*Dinitroquinol.*—The monoacetate (5 g.), dissolved in methanol (50 ml.), was stirred with 10% aqueous sodium carbonate (500 ml.). After an hour the deep violet solution was made strongly acid with concentrated hydrochloric acid, then extracted with ether, and after the ether extracts had been dried and evaporated the yellow quinol was crystallised twice from water, forming needles m. p. 136—138° (Found: C, 36·5, 36·1; H, 1·9, 1·9; N, 14·1, 14·1. Calc. for $C_6H_4N_2O_6$: C, 36·0; H, 2·0; N, 14·0%). Thus no water of crystallisation was found. The 2,6-dinitro-structure was confirmed by the infrared analysis above.

Oxidation of 2,6-*Dinitroquinol.*—(*a*) Nitrogen oxides were added to a stirred suspension of the quinol in carbon tetrachloride. The liquid became green and frothed vigorously, producing a brown gum. This was extracted in hot chloroform, affording a low yield of yellow crystals on cooling and these were recrystallised. Unlike the quinol they did not give violet colours with sodium carbonate or hydroxide solution, nor did they produce colours with mesitylene, durene, or hexamethylbenzene. Aqueous solutions were red and strongly acid. Infrared spectra showed only weak, broad absorptions at 3460 cm.$^{-1}$ (possibly OH hydrogen-bonded), no absorption in the 2950 cm.$^{-1}$ region (no CH), and a strong absorption at 1695 cm.$^{-1}$ (C=O, probably benzoquinone). These confirm the structure (III) (nitranilic acid) for this material (Found: N, 12·3. Calc. for $C_6H_2N_2O_8$: N, 12·2%). The substance exploded when heated.

(*b*) To the quinol (100 mg.) in dichloromethane (50 ml.) containing molecular sieve type 5A (10 g.), cooled in acetone–ice, were added nitrogen oxides (0·3 ml.). The suspension was stirred in the absence of moisture for 30 min. The oxides, which interfered with spectra of mixtures containing durene, pentamethylbenzene, and hexamethylbenzene, were removed by degassing

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[4] Brook, *J.*, 1952, 5040.

[5] Nietzki, (*a*) *Ber.*, 1878, **11**, 470; (*b*) *Annalen*, 1882, **215**, 141.

[6] Richter, *Ber.*, 1913, **46**, 3434.

at room temperature on a water-pump for 10 min. For the lower hydrocarbons (toluene and mesitylene), this solution was used directly whereas for the others it was diluted (1 : 10) and a large excess of hydrocarbon was added. The colours of all mixtures deteriorated considerably in 15 min. at room temperature. So the benzoquinone was stored at $-30°$ and was allowed to warm only during the absorption studies, and solutions of identical benzoquinone concentrations, prepared simultaneously, were used in the observed and the compensating beam of the measuring instrument.

In these conditions a series of broad absorption bands was produced with the methylbenzenes in the order expected for charge-transfer complex formation.

Attempts to isolate the benzoquinone by evaporation of the dichloromethane at low temperature produced a yellow gum which exploded at room temperature. This is not necessarily a property of dinitrobenzoquinone for similar results were obtained [3] on evaporating oxidised solutions of cyano- and nitro-quinol; rather it is a hazard of oxidation by nitrogen oxides, and isolation of products by this method should be avoided.

Isolation of Solid Complexes.—When hot solutions of 2,3-dicyanobenzoquinone (1 g.) and hexamethylbenzene (1 g.) in acetic acid (100 ml.) or of 2,3-dichloro-5,6-dicyanobenzoquinone (0·45 g.) and durene (0·3 g.) in the acid (10 ml.) were cooled, black crystals were deposited. It was not possible to recrystallise these, presumably because they dissociated to the components; hence they were formed by using the purest materials as described above. The vacuum-dried crystals gave analyses for the 1 : 1 *complexes* (Found, for dicyanobenzoquinone–hexamethylbenzene: C, 74·9; H, 6·3; N, 8·6. $C_{20}H_{20}N_2O_2$ requires C, 75·0; H, 6·25; N, 8·75%. Found, for dichlorodicyanobenzoquinone–durene: C, 60·6; H, 4·0; N, 7·75. $C_{18}H_{14}Cl_2N_2O_2$ requires C, 59·8; H, 3·9; N, 7·8%). Neither complex melted below 320°. The dicyanobenzoquinone–hexamethylbenzene complex became a light brown below 120° and had darkened again at 170°, and sublimation of white crystals occurred.

Solvents.—Measurements were made on $\sim 10^{-4}$M-benzoquinone solutions in carbon tetrachloride and dichloromethane. Inconsistent results were obtained with " AnalaR " carbon tetrachloride and were ascribed to the water content of the solvent with which the benzoquinones reacted. The highest and most consistent results were obtained with solvents treated overnight with " molecular sieve " type 5A (30 g./2 l.), filtered, and fractionally distilled.

Visible and ultraviolet spectra were recorded on a Cary spectrophotometer in 10 cm. cells, with a cell compartment encased in a water-jacket controlled to $\pm 0{\cdot}25°$. With the exception of the dinitrobenzoquinone, benzoquinone absorptions were negligible in the region of the charge-transfer bands and compensation was not necessary.

Nuclear magnetic resonance spectra were measured in spinning glass tubes of 5 mm. outside diameter on a Perkin-Elmer 40 Mc. spectrometer.

Infrared spectra were measured for Nujol and hexachlorobutadiene mulls on a Perkin-Elmer model 21 spectrometer.

Electron spin resonance spectra were recorded on a Varian 100 Kc./V4500—10A spectrometer with the Varian 6 in. magnet and power supply.

RESULTS AND DISCUSSION

Ultraviolet and Visible Spectra.—Colours were produced immediately on mixing solutions containing the benzoquinones and the hydrocarbons which were not possessed by either component separately. These were ascribed to the reversible formation of loose molecular complexes, for deviations from Beer's law were observed, and in dichloromethane and carbon tetrachloride the standard Benesi-Hildebrand type relation [7] of the form

$$\frac{b\alpha}{D} = \frac{b}{\varepsilon} + \frac{1}{K\varepsilon} \qquad (1)$$

[where α is the constant acceptor concentration, b the varied donor concentration ($b \gg \alpha$), D the optical density for a 1 cm. light path here taken at maximum absorption, ε the molar absorbance for the complex, and K (in l. mole^{-1} units) is the association constant for complex formation], was followed closely, implying 1 : 1 complex formation.

The values for the positions of maxima of the single, broad bands, association constants,

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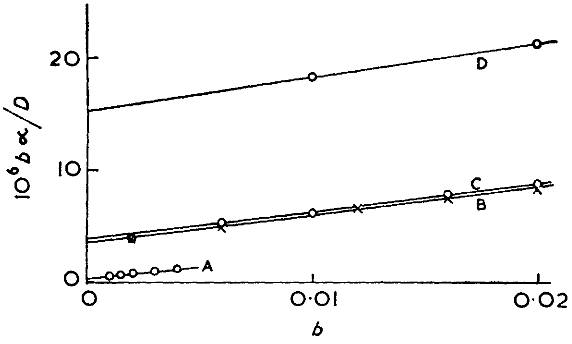
[7] Benesi and Hildebrand, *J. Amer. Chem. Soc.*, 1949, **71**, 2703.

molar absorbances, and heats of association are shown in Table 1. The values of ΔH were estimated by repeating one of the measurements of optical density at 50° and assuming the same value of molar absorbance for the complex applied at this temperature. When the solutions were cooled to 25° only the dicyanobenzoquinone measurements were reproducible and it must be concluded that the dichlorodicyanobenzoquinone either reacted partially with the donors at the elevated temperature or decomposed. Again the sensitivity of these molecules to traces of water and of the complexes to light makes very accurate measurements difficult. The method of estimating the constants of equation (1) from the slopes and intercepts of the plots of $b\alpha/D$ against b imply that even if α is uncertain the measured value of K is not altered. The accuracy of ε only is suspect.



Benesi–Hildebrand plots for carbon tetrachloride solutions containing complexes between (A) dichlorodicyanobenzoquinone and hexamethylbenzene, (B) dichlorodicyanobenzoquinone and durene, (C) dicyanobenzoquinone and hexamethylbenzene, (D) dichlorodicyanobenzoquinone and mesitylene.

Plots of the energy of maximum absorption of the bands against the lowest ionisation potential of the donor are reasonably linear, with *p*-xylene and durene lying furthest from the lines. The empirical relations in electron volts are:

$$\nu_{\text{max.}} = 0{\cdot}75 I_{\text{D}} - 3{\cdot}67 \qquad \text{(Dicyanobenzoquinone)} \qquad (2)$$

$$\nu_{\text{max.}} = 0{\cdot}69 I_{\text{D}} - 3{\cdot}38 \qquad \text{(Dichlorodicyanobenzoquinone)} \qquad (3)$$

$$\nu_{\text{max.}} = 0{\cdot}79 I_{\text{D}} - 4{\cdot}01 \qquad \text{(Dinitrobenzoquinone)} \qquad (4)$$

The positions of absorption follow the charge-transfer bands of tetracyanoethylene complexes [8] although the correlations [9] are not closer than the correlations in the equations above. Also the three values of free energy of complex-formation obtainable from Table 1 for dicyanobenzoquinone are linearly related to donor ionization potential [8] whereas the values for the dichlorodicyanobenzoquinone complexes, although in the same order, are not.

The colours observed may therefore be assigned to the class of π–π charge-transfer transitions.[10]

A study of the complex-formation in cyclohexane at room temperature showed that the ultraviolet absorption spectra of mixtures of hexamethylbenzene with the benzoquinones (I) and (II) were the same as the sum of their components. Low-temperature measurements, which have demonstrated interesting effects on the tetracyanoethylene–hexamethylbenzene complex,[11] have not been attempted. Small changes in the position of absorption (~5 mμ) were found for donor concentrations greater than 0·4M. This was attributed to the effect of changed solvent composition on the energy of the transition. The complexes of hexamethylbenzene have a greater association constant in carbon tetrachloride (a solvent of weak acceptor properties [12]) than in dichloromethane as measured from equation (1). This has been observed in other cases. This is contrary to expectation

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[8] Merrifield and Phillips, *J. Amer. Chem. Soc.*, 1958, **80**, 2778.

[9] Foster, *Nature*, 1958, **181**, 337.

[10] Mulliken, *J. Amer. Chem. Soc.*, 1952, **74**, 811; *J. Phys. Chem.*, 1952, **56**, 801.

[11] Czekalla, *Z. Elektrochem.*, 1959, **63**, 1157.

[12] Stevenson and Coppinger, *J. Amer. Chem. Soc.*, 1962, **84**, 149; Strieter and Templeton, *J. Chem. Phys.*, 1962, **37**, 161.

TABLE 1.

Complex formation of benzoquinones with methylbenzenes.

Abbreviations: DCQ, 2,3-dicyanobenzoquinone; DC^{2}Q, 2,3-dichloro-5,6-dicyanobenzoquinone; DNQ, 2,6-dinitrobenzoquinone; HMB, PMB, D, M, *o*-X, *m*-X, *p*-X, T, hexamethylbenzene, pentamethylbenzene, durene, mesitylene, etc.

Carbon tetrachloride, 25°.

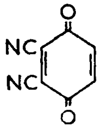
DCQ:	HMB	D	M	DC^{2}Q:	HMB	D	M
$\lambda_{max.}$ (mμ)	573	538	470		615	585	506
K	73·8	12·3	4·9		574	72·3	19·2
$10^{-3}\varepsilon$	3·85	3·00	2·30		4·91	4·00	3·40
ΔH (kcal. mole^{-1})	7·75	6·85	5·08		—	—	—

Dichloromethane.

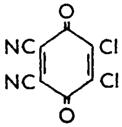
DCQ, 22°:	HMB	PMB	D	M	*o*-X	*m*-X	*p*-X	T
$\lambda_{max.}$	581	551	543	477	452	451	486	420
K	13·4	—	—	—	—	—	—	—
$10^{-3}\varepsilon$	3·49	—	—	—	—	—	—	—
DC^{2}Q, 22°:								
$\lambda_{max.}$	629	596	595	518	485	485	526	459
K	97·5	—	—	—	—	—	—	—
$10^{-3}\varepsilon$	3·26	—	—	—	—	—	—	—
DNQ, 10°:								
$\lambda_{max.}$	586	554	545	478	428	458	501	424

for a solvent effect arising from a competition between the solvent and acceptor for the donor. A possible explanation is that dichloromethane is a better solvating agent for the polar benzoquinone molecules.

There must be some doubt as to the identity of the species existing in the oxidised dinitroquinol solutions. Its manner of preparation, its instability, and the fact that it is a strong acceptor support the structure (IV). On the other hand, the benzoquinones (I) and (II) are readily decomposed by water and the isolation of nitranilic acid (III) during the oxidation implies that the 2,6-dinitrobenzoquinone (IV) is also: Colours were not observed with nitranilic acid and hydrocarbons, but it is possible that the results in Table 1 arise from a monohydroxy-2,6-dinitrobenzoquinone and this is supported by the closeness in positions of the charge-transfer bands of the hydrocarbons for this acceptor with the same bands for dicyanobenzoquinone. Table 2 shows that replacement of a cyano- by a nitro-group in a monosubstituted benzoquinone (structures V and VI) moves the absorption of the hexamethylbenzene charge-transfer complex considerably to longer wavelength and the absorption for complexes of the benzoquinone (IV) might be expected to appear well beyond those of the dicyanobenzoquinone. Care was taken to remove water, however; and, since 2,6-dinitrobenzoquinone is being compared with the 2,3-dicyanobenzoquinone, where it is doubtful that electronic effects may be simply extrapolated from the mono-derivatives, it is probable that observations were made on solutions containing the compound (IV).



(I)



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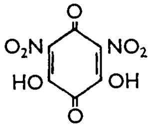
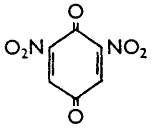
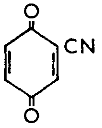


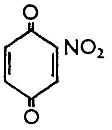
(III)



(IV)



(V)



(VI)

TABLE 2.

Charge-transfer bands of some benzoquinone–hexamethylbenzene complexes in dichloromethane.

Benzoquinone	Cyano-	Nitro-	2,3-Dicyano-	Supposed 2,6-dinitro-
$\lambda_{max.}$ (mμ)	470	514	581	586

Comparison of Table 1 with similar studies on tetracyanoethylene[8] shows that the benzoquinones are comparable in acceptor strength with this compound and investigations of their chemistry may therefore be of interest. Tetracyanobenzoquinone [13] is expected to be a still stronger acceptor than the compounds mentioned above. The instability of the dinitro- and mononitro-benzoquinones [3] indicates that the preparation of the tetranitro-compound will prove difficult.

Isolation and Properties of the Complexes.—Stable complexes were isolated only in the cases of dicyanobenzoquinone–hexamethylbenzene and dichlorodicyanobenzoquinone–durene. Pfeiffer's [14] procedure gave black, iridescent crystals, which in solution produced the absorptions above. No definite melting points were obtained from these below 320°, *i.e.*, well above the melting points of the constituents. The colours of both the solids and carbon tetrachloride solutions of the hexamethylbenzene, durene, and mesitylene complexes faded during several days in diffuse sunlight. With the exception of the hexamethylbenzene–dichlorodicyanobenzoquinone, which faded in 4 days in the absence of light, they were stable in the dark. The crystals showed strong electron spin resonance absorption, which, in conjunction with the marked changes in infrared spectra, indicates [15] that positive and negative ion radicals may be trapped in the lattices. The infrared spectra of the freshly prepared, dried crystals showed considerable differences from those of the constituents, for although a few of the absorptions could have been perturbations of the benzoquinone spectra (peaks at 992 and 843 cm.$^{-1}$ in dicyanobenzoquinone were replaced by peaks at 980 and 820 cm.$^{-1}$ in the hexamethylbenzene complex, whereas peaks at 800 and 720 cm.$^{-1}$ in dicyanodichlorobenzoquinone were replaced by others at 790 and 710 cm.$^{-1}$ in the durene complex), many of the absorptions could not be attributed to either component (3295, 1500, 1460, 1283, 1035 in the first complex; 3250, 1428, 1197, 1080 cm.$^{-1}$ in the second).

Several authors have observed small changes in chemical shifts in the nuclear magnetic resonance spectra of mixtures [16] in which acceptor–donor type interactions can occur. A study of concentrated solutions of the strong acceptors, 2,3-dicyanobenzoquinone (0·5M), 2,3-dichloro-5,6-dicyanobenzoquinone (1·0M), and tetracyanoethylene (2·3M) in the reasonably strong π-donor mesitylene showed only very small increases in the τ values of the lower proton band in comparison with the neat solvent (7·2M). No changes were observed in the methyl band with respect to tetramethylsilane or cyclohexane internal standard, nor were there changes in fine structure. The increases were a little more than one cycle (1·4, 1·3, and 1·3 for the order of the acceptors above in comparison with an experimental accuracy of about $\pm$0·4 cycle). A simple interpretation, among others,[17] of the direction of shift is as follows. By means of the ring-current effect.[18] it is the π-electrons which are responsible for low values of the screening constants of the aromatic protons; hence their implication in forming complexes may produce increases in shielding values. On the other hand, changes in magnitude of the charge effect [19] should be in opposition to this; hence the resulting alterations in resonance position may well be small.

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[14] Pfeifer, *Annalen*, 1916, **412**, 253.

[15] Bijl, Kainer, and Rose-Innes, *J. Chem. Phys.*, 1959, **30**, 765; Matsunaga and McDowell, *Nature*, 1960, **185**, 916; Kainer and Otting, *Chem. Ber.*, 1955, **88**, 1921; Eastman, Androes, and Calvin, *J. Chem. Phys.*, 1962, **36**, 1197.

[16] Korinek and Schneider, *Canad. J. Chem.*, 1957, **35**, 1157; Coyle and Stone, *J. Amer. Chem. Soc.*, 1961, **83**, 4138; Schug and Martin, *J. Phys. Chem.*, 1962, **66**, 1554; Creswell and Allred, *ibid.*, p. 1469.

[17] Buckingham, Schaefer, and Schneider, *J. Chem. Phys.*, 1960, **32**, 1227.

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[19] Fraenkel, Carter, McLachlan, and Richards, *J. Amer. Chem. Soc.*, 1960, **82**, 5846.