# 755. *Interaction of Lewis Acids with Aromatic Hydrocarbons and Bases. Part XVII.* The Association of Hexamethylbenzene with Substituted* p-*Benzoquinones in Carbon Tetrachloride Solution.*

By R. Foster, D. Ll. Hammick, and P. J. Placito.

The degree of interaction of hexamethylbenzene with a series of substituted *p*-benzoquinones in carbon tetrachloride solution has been determined colorimetrically. The relation between the free energies of the interaction, evaluated from the association constants, and the energies of excitation of the complexes is discussed in the light of Mulliken's [1] concept for charge-transfer complexes.

In a previous communication [2] a relation between the ionisation potential of an electron donor and the free energy of complex formation by the donor with electron-accepting molecules was demonstrated. For a series of methylbenzenes interacting with chloranil in *cyclo*hexane solution, it was found that there is a linear relation between the ionisation potential of the electron donor and the free energy of formation of the complex, and also between the ionisation potential of the electron donor and the energy of excitation of the complex as measured by the wave-number of the maximum of the charge-transfer band. In the present communication, the effect of varying the acceptor component of the complex has been studied. Hexamethylbenzene was chosen as the donor since it has already been shown to be a powerful Lewis base in this type of interaction.[2,3]

The degree of association of hexamethylbenzene with a series of substituted *p*-benzoquinones has been determined spectroscopically. It has been assumed that the complexes are all of the charge-transfer type described by Mulliken,[1] in which the concentrations of the complexes may be determined by the intensities of the absorption bands which are characteristic of the complexes themselves. The algebraic method of evaluating the association constants used is that described by McConnell and his co-workers,[4] in which allowance is made for the absorption due to uncomplexed acceptor molecules. The method of evaluation also gives values of the molecular extinction coefficients of the complexes at the wavelength at which the determinations are made.

## EXPERIMENTAL

*Preparation and Purification of Materials.—Carbon tetrachloride.* The " AnalaR " reagent, purified by the method of Gunther, von der Horst, and Cronheim,[5] had $n_D^{19}$ 1·4604—1·4606, b. p. 76·0—76·5°/756 mm.; Gunther *et al.* give $n_D^{19\cdot5}$ 1·46040, b. p. 76·71°/760 mm.

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* Part XVI, *J.*, 1956, 555.

[1] (*a*) Mulliken, *J. Amer. Chem. Soc.*, 1950, **72**, 605; (*b*) *ibid.*, 1952, **74**, 811; (*c*) *J. Phys. Chem.*, 1952, **56**, 801.

[2] Foster, Hammick, and Parsons, *J.*, 1956, 555.

[3] Briegleb and Czekalla, *Z. Electrochem.*, 1954, **58**, 249.

[4] (*a*) Laudauer and McConnell, *J. Amer. Chem. Soc.*, 1952, **74**, 1221; (*b*) Lawrey and McConnell, *ibid.*, p. 6175.

[5] Gunther, von der Horst, and Cronheim, *Z. Electrochem.*, 1928, **34**, 616.

*Hexamethylbenzene.* Sublimed twice, and then recrystallised twice from ethanol, this had m. p. 162·5—163·5°. Briegleb and Czekalla [3] give m. p. 164·5°.

*Chloranil.* Recrystallised four times from benzene, this formed yellow plates, m. p. (sealed tube) 289° (Graebe [6] gives m. p. 290°).

p-*Benzoquinone.* Recrystallised twice from chloroform, the quinone formed orange prisms, m. p. 112·7°. Another sample was sublimed three times, as yellow needles, m. p. 113·5°. Hassel and Naeshagen [7] give m. p. 116·5°; Hammick Hampson, and Jenkins [8] give m. p. 112·8—113·6°; Briegleb and Czekalla [3] give m. p. 113·5°.

*Toluquinone.* Two recrystallisations from ethanol, rapid drying and storage *in vacuo* gave bronze plates and needles, m. p. 67·5°; Nietzski [9] gives m. p. 67°, Carstanjen [10] m. p. 69°.

2 : 6-*Dimethyl*-p-*benzoquinone.*—Recrystallisation from water–ethanol (8 : 1) gave bright yellow needles, m. p. 72° (sealed tube). Noelting and Baumann [11] give m. p. 72—73°.

*Bromanil.* Prepared as described by Graebe and Weltner [12] and recrystallised twice from benzene, this was obtained as lustrous deep yellow plates, m. p. (sealed tube) 300° (decomp.). Graebe and Weltner [12] give m. p. 300°.

*Iodanil.* Prepared as described by Torrey and Hunter [13] and repeatedly recrystallised from ethyl acetate to constant m. p., this quinone had m. p. (sealed tube) 290° (decomp.). Torrey and Hunter give m. p. 282—284°.

2 : 6-*Dichloro*-p-*benzoquinone.* Prepared as described by Faust [14] and crystallised twice from ethanol, this had m. p. 120°. Faust gives m. p. 120°.

*Chloro*-p-*benzoquinone.*—Prepared as described by Conant and Fieser [15] and recrystallised three times from ethanol, this formed orange prisms and a yellow amorphous powder, m. p. (both forms) 56·5°. Conant and Fieser give m. p. 57°.

*Duroquinone.*—Prepared as described by Smith [16] and recrystallised three times from aqueous ethanol, this formed yellow needles, m. p. 111°. Smith gives m. p. 109—110°, Nef [17] m. p. 111°.

*Method of Evaluating the Association Constants of the Interactions.*—The method described by McConnell and his co-workers,[4] which has been used to determine the association constants. It is fundamentally the same as those described by Benesi and Hildebrand [18] and Foster, Hammick, and Wardley,[19] except that allowance can be made in the first method for systems in which the absorption of the acceptor is measurable at the wavelength at which the determinations are made. In the system chloranil–hexamethylbenzene in carbon tetrachloride solution, the absorption of both components is zero at the wavelength of maximum absorption of the complex. This example thus permits a comparison to be made between the three methods when the determination is made at this wavelength. Some results are given in Table 1.

TABLE 1. *Extinction coefficient* ($\varepsilon_1$), *association constant* ($K$), *and free energy of formation* ($\Delta G$) *of the complex hexamethylbenzene–chloranil in carbon tetrachloride solution, determined by three methods from the same data.*

| | $\varepsilon_1$ (l. mole$^{-1}$ cm.$^{-1}$) | $K$ (l. mole$^{-1}$) | $\Delta G$ (kcal. mole$^{-1}$) |
|---|---|---|---|
| Benesi and Hildebrand | 2470 | 11·0 | −1·39 |
| Foster, Hammick, and Wardley | 2490 | 10·6 | −1·38 |
| McConnell and co-workers | 2510 | 10·7 | −1·37 |

The derivation of the function used to evaluate the association constant and the extinction coefficient of the complex given by McConnell and his co-workers [4] is not easy to follow. We give the following clarification.

The method can be applied only to systems in which the donor (*b*) does not absorb at the

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[6] Graebe, *Annalen*, 1891, **263**, 19.
[7] Hassel and Naeshagen, *Z. phys. Chem.*, 1929, **6**, *B*, 445.
[8] Hammick, Hampson, and Jenkins, *J.*, 1938, 1263.
[9] Nietzki, *Ber.*, 1877, **10**, 834.
[10] Carstanjen, *J. prakt. Chem.*, 1881, **23**, 423.
[11] Noelting and Baumann, *Ber.*, 1885, **18**, 1151.
[12] Graebe and Weltner, *Annalen*, 1891, **263**, 31.
[13] Torrey and Hunter, *J. Amer. Chem. Soc.*, 1912, **34**, 708.
[14] Faust, *Annalen*, 1869, **149**, 153.
[15] Conant and Fieser, *J. Amer. Chem. Soc.*, 1923, **45**, 2204.
[16] Smith, *Org. Synth.*, Coll. Vol. II, p. 254.
[17] Nef, *Ber.*, 1885, **18**, 2807.
[18] Benesi and Hildebrand, *J. Amer. Chem. Soc.*, 1949, **71**, 2703.
[19] Foster, Hammick, and Wardley, *J.*, 1953, 3817.

wavelength at which the measurements are made, though the acceptor ($a$) may absorb at this wavelength. If the optical density of a solution of the complex containing a total concentration of acceptor (*i.e.*, free and complexed) $= \alpha$ is $D$ cm.$^{-1}$, then $\bar{\varepsilon}$, the "formal extinction coefficient" of the solution, is defined by :

$$\bar{\varepsilon} = D/\alpha \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$\bar{\varepsilon}$ will become greater as $b$ is increased in accordance with the complexing equilibrium $a + b \rightleftharpoons c$.

The equilibrium constant for this interaction is given by

$$K = [c]/[a][b] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$[c]$, $[a]$, and $[b]$ represent the concentrations at equilibrium Now if $\varepsilon_0$ is the extinction coefficient of the acceptor, and $\varepsilon_1$ is the extinction coefficient of the complex, equation (1) gives :

$$D = \bar{\varepsilon}\alpha = \varepsilon_0[a] + \varepsilon_1[c] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

also

$$\alpha = [a] + [a][b]K = [a](1 + K[b]) \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

A function $Q$ may be defined such that :

$$Q = \frac{[b]}{(\bar{\varepsilon} - \varepsilon_0)} = \frac{1 + K[b]}{(\varepsilon_1 - \varepsilon_0)K}$$

from equations 2, 3, and 4. If $[b] \gg [a]$, then $[b]$ may be assumed to have the same value as the concentration of $b$ originally added.

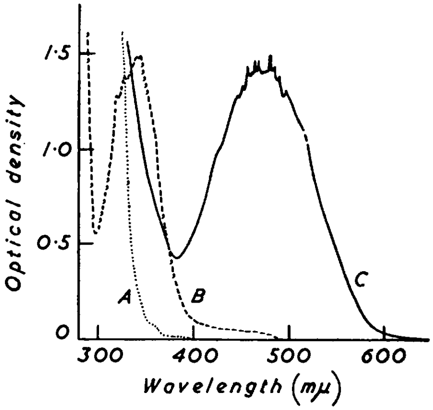


FIG. 1. *Absorption spectra in carbon tetrachloride of*: *A*, *hexamethylbenzene* (0·428M); *B*, 2 : 6-*dichloro*-p-*benzoquinone* (0·00335M); *C*, *a mixture of hexamethylbenzene* (0·428M) *and* 2 : 6-*dichloro*-p-*benzoquinone* (0·00335M).

Thus a plot of $Q$ against $[b]$ as abscissa should be linear, the gradient of the line being equal to $1/(\varepsilon_1 - \varepsilon_0)$ and the intercept with the $Q$ axis $1/(\varepsilon_1 - \varepsilon_0)K$, whence $K$ and $\varepsilon_1$ may be found.

Similarly if there is complexing of the type $ab_2$ present as well as of the type $ab$, then it may be shown that :

$$Q = \frac{1 + K_1[b] + K_2[b]^2}{(\varepsilon_1 - \varepsilon_0)K_1 + (\varepsilon_2 - \varepsilon_0)K_2[b]}$$

where $K_1$ is the equilibrium constant of the 1 : 1 complex, and $K_2$ that of the 1 : 2 complex, and $\varepsilon_1$ and $\varepsilon_2$ the extinction coefficients of the two complexes.

In none of the systems examined do the data yield significant values for $K_2[b]^2$ and it is therefore to be concluded that interactions other than 1 : 1 are negligible.

*Details of the Determination of the Association Constant and Extinction Coefficient of the Complex* 2 : 6-*Dichloro*-p-*benzoquinone–Hexamethylbenzene in Carbon Tetrachloride Solution.*—The McConnell method does not require that the measurements of optical density be made at the wavelength of maximum absorption of the complex. Nevertheless it is preferable to work at this wavelength, since there $D$ is usually a maximum for given concentrations of the two components. Also the value of the extinction coefficient of the complex is immediately obtainable, though in fact the charge-transfer bands do show some fine structure so that the wavelength of maximum absorption may not coincide with the centre of the band.

TABLE 2. *Data for the determination of the constants of the complex hexamethylbenzene–2 : 6-dichloro-*p*-benzoquinone in carbon tetrachloride solution.*

Master solutions : hexamethylbenzene 0·4919M ; 2 : 6-dichloro-*p*-benzoquinone 0·00245M.
Temperature : 290·4° K. Wavelength : 480 mμ. $[a] = \alpha = 0{\cdot}00070$M.
Optical density of acceptor solution (0·00245M) was 0·016 cm.$^{-1}$, whence $\varepsilon_0 = 6{\cdot}6$.

| $[b]$ (M) | $D$ (cm.$^{-1}$) | $D/\alpha = \bar{\varepsilon}$ | $\bar{\varepsilon} - \varepsilon_0$ | $\dfrac{10^3\,[b]}{(\bar{\varepsilon} - \varepsilon_0)}$ | $[b]$ (M) | $D$ (cm.$^{-1}$) | $D/\alpha = \varepsilon$ | $\bar{\varepsilon} - \varepsilon_0$ | $\dfrac{10^3\,[b]}{(\bar{\varepsilon} - \varepsilon_0)}$ |
|---|---|---|---|---|---|---|---|---|---|
| 0·0703 | 0·274 | 391·6 | 385·0 | 0·1826 | 0·2109 | 0·607 | 867·6 | 861·0 | 0·2452 |
| 0·1054 | 0·371 | 530·3 | 523·7 | 0·2013 | 0·2460 | 0·659 | 941·7 | 935·1 | 0·2632 |
| 0·1406 | 0·457 | 652·7 | 646·1 | 0·2178 | 0·2812 | 0·708 | 1012·0 | 1005·4 | 0·2799 |
| 0·1757 | 0·531 | 579·1 | 752·5 | 0·2334 | 0·3515 | 0·807 | 1153·0 | 1146·4 | 0·3069 |

TABLE 3. *Summarised results for association constants (K), free energies of formation (ΔG), molar extinction coefficients ($\varepsilon_1$), and wave-numbers (ν) of the maxima of the charge-transfer band-envelopes of hexamethylbenzene–substituted* p*-benzoquinone complexes in carbon tetrachloride solution.*

| Acceptor | Temp. (°K) | $K$ (l./mole) | $\Delta G$ (kcal./mole) | $\varepsilon_1$ | $\nu$ (cm.$^{-1}$) | Reduction potential [a] (V) |
|---|---|---|---|---|---|---|
| Chloranil | 291·0° | 10·79 | −1·375 | 2502 | | |
| | 291·5 | 10·01 | −1·333 | 2540 | | |
| | 291·0 | 10·33 | −1·350 | 2528 | | |
| | 291·5 | 10·50 | −1·361 | 2517 | | |
| | 291·5 | 10·81 | −1·377 | 2487 | | |
| | 289·0 | 9·83 | −1·252 | 2732 | | |
| | 291·0 | 10·64 | −1·366 | 2522 | 19,300 [b] | 0·742 |
| Means ...... | — | 10·27 ± 0·38 [b] | −1·345 ± 0·040 [b] | 2548 ± 77 [b] | | |
| Bromanil | 289·0 | 5·84 | −1·013 | 2325 | | |
| | 291·9 | 7·02 | −1·129 | 1822 | | |
| | 290·8 | 6·09 | −1·044 | 2070 | | |
| | 292·2 | 5·88 | −1·016 | 2627 | | |
| | 290·0 | 7·33 | −1·147 | 1666 | | |
| | 290·0 | 6·81 | −1·105 | 1725 | | |
| | 290·0 | 7·63 | −1·170 | 1620 | 18,980 | 0·746 |
| Means ...... | — | 6·66 ± 0·69 | −1·091 ± 0·059 | 1979 ± 351 | | |
| Iodanil | 289·4 | 3·51 | −0·728 | 1541 | | |
| | 290·0 | 3·72 | −0·757 | 1366 | 19,570 | — |
| Means ...... | — | 3·62 ± 0·10 | −0·742 ± 0·015 | 1454 ± 88 | | |
| 2 : 6-Dichloro-*p*-benzoquinone | 290·4 | 2·87 | −0·606 | 2273 | | |
| | 290·4 | 2·81 | −0·597 | 2276 | | |
| | 292·2 | 2·42 | −0·513 | 2408 | | |
| | 292·2 | 2·28 | −0·480 | 2516 | 20,830 | 0·740 |
| Means ...... | — | 2·60 ± 0·25 | −0·549 ± 0·054 | 2370 ± 101 | | |
| Chloro-*p*-benzoquinone | 292·0 | 1·45 | −0·218 | 1838 | | |
| | 291·0 | 1·27 | −0·137 | 2087 | | |
| | 291·0 | 1·38 | −0·184 | 1978 | 22,620 | 0·734 |
| Means ...... | — | 1·37 ± 0·08 | +0·180 ± 0·033 | 1968 ± 102 | | |
| *p*-Benzoquinone | 290·8 | 0·61 | +0·286 | 1944 | | |
| | 291·6 | 0·56 | +0·336 | 2089 | 23,920 | 0·711 |
| Means ...... | — | 0·58 ± 0·02 | +0·311 ± 0·025 | 2016 ± 73 | | |
| Methyl-*p*-benzoquinone | 291·2 | 0·49 | +0·440 | 1820 | 24,450 | 0·653 |
| | 291·0 | 0·51 | +0·395 | 1732 | | |
| Means ...... | — | 0·50 ± 0·01 | +0·418 ± 0·022 | 1776 ± 44 | | |
| 2 : 6-Dimethyl-*p*-benzoquinone | 288·8 | 0·35 | +0·599 | 2117 | | |
| | 289·0 | 0·34 | +0·622 | 2141 | 25,640 | 0·607 |
| Means ...... | — | 0·34 ± 0·01 | +0·610 ± 0·012 | 2129 ± 12 | | |
| Duroquinone | 289·0 | 0·32 | +0·665 | 1414 | | |
| | 288·0 | 0·50 | +0·405 | 969 | | |
| | 290·0 | 0·42 | +0·522 | 1145 | 25,440 | — |
| Means ...... | — | 0·41 ± 0·07 | +0·531 ± 0·106 | 1176 ± 183 | | |

[a] Relative potentials in benzene solution determined by Hunter and Kvalnes (*J. Amer. Chem. Soc.*, 1932, **54**, 2878) and Kvalnes (*ibid.*, 1934, **56**, 668, 671). [b] Briegleb and Czekalla[3] give $K = 9{\cdot}25$ l. mole$^{-1}$, $\Delta G = -1{\cdot}36$ kcal. mole$^{-1}$, $\nu = 19{,}350$ cm.$^{-1}$, and $\epsilon_1 = 2750$.

Three separate spectra are measured (cf. Fig. 1) : (1) the spectrum of the donor, hexamethylbenzene, in carbon tetrachloride (this shows that the absorption is negligible above 360 mμ); (2) the spectrum of the acceptor, 2 : 6-dichloro-*p*-benzoquinone in carbon tetrachloride, from which $\varepsilon_0$ may be calculated; and (3) the spectrum of a mixture of donor and acceptor in carbon tetrachloride in which $[\alpha] \ll [b]$ (this shows a new band with a maximum at about 480 mμ).

Two master solutions were prepared, one of pure acceptor, the other of pure donor, and from them eight solutions, containing a fixed concentration of acceptor and varying amounts of donor were made up volumetrically into calibrated flasks. Each solution had a large donor concentration relative to that of acceptor. The optical densities ($D$) of this set of solutions were then measured at 480 mμ, by means of a Unicam S.P. 600 Spectrophotometer. The results of a typical determination are given in Table 2. The linear relation between $Q$ and $b$ was determined statistically by the method of least squares, whence the gradient $= 4{\cdot}41 \times 10^{-4}$ cm. mole l.$^{-1}$, and the intercept with the $Q$ axis $= 1{\cdot}56 \times 10^{-4}$ cm. mole$^2$ l.$^{-2}$.

As $\varepsilon_0 = 6{\cdot}6$ l. mole$^{-1}$ cm.$^{-1}$, $\varepsilon_1 = 2276$ l. mole$^{-1}$ cm.$^{-1}$, and $K = 2{\cdot}82$ l. mole$^{-1}$.

The results of all the determinations are summarised in Table 3.

## DISCUSSION

The free energies of formation of the hexamethylbenzene–substituted *p*-benzoquinone complexes are not linearly related to the reduction potentials of the quinones themselves (cols. 4 and 7 of Table 3). This is to be expected since the free energies of formation of the complexes are the sum of the contributions due to polarisation, London, van der Waals, and other such forces, further stabilised by resonance with a structure in which one, or perhaps two, electrons have been donated from the donor to the acceptor molecule. The reduction potentials of the quinones on the other hand are a measure of the free energies involved in the acceptance of a pair of hydrogen atoms. Nevertheless the free energies of formation of the quinone complexes derived from our determinations of equilibrium constants are in approximately the same order as the reduction potentials of the corresponding *p*-benzoquinones.

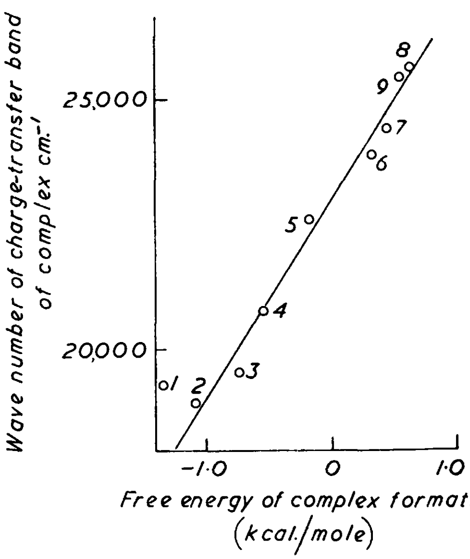


FIG. 2. *Relation between the free energy of complex formation* ($\Delta G$) *and the wave-number of the charge-transfer band* ($\nu$) *for the series of hexamethylbenzene–substituted* p-*benzoquinone complexes in carbon tetrachloride.* 1, *Chloranil*; 2, *bromanil*; 3, *iodanil*; 4, 2 : 6-*dichloro*-p-*benzoquinone*; 5, *chloro*-p-*benzoquinone*; 6, p-*benzoquinone*; 7, *methyl*-p-*benzoquinone*; 8, 2 : 6-*dimethyl*-p-*benzoquinone*; 9, *duroquinone*.

It is seen that the energy of excitation of each complex as measured by the wave-number of the central peak of the charge-transfer band is proportional to the free energy of formation of the complex (Fig. 2). This may be explained in terms of Mulliken's [1] description of this class of complex. The ground state of the complex is $\psi_N$ where :

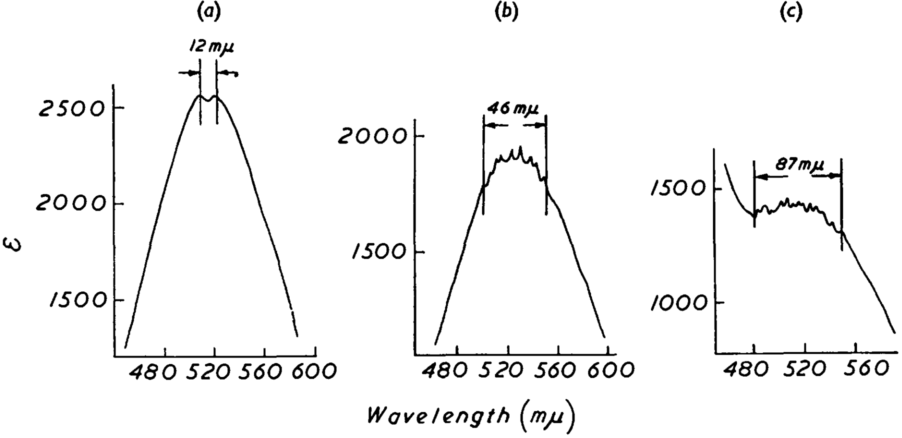
$$\psi_N = x\psi(a, b) + y\psi(a^-{-}b^+)$$

$a$ and $b$ represent the electron donor and the electron acceptor respectively. $\psi(a, b)$ is a no-bond function, and $\psi(a^{-}–b^{+})$ is the dative function in which an electron has been donated from $b$ to $a$. An excited state $\psi_{\mathrm{E}}$ exists where :

$$\psi_{\mathrm{E}} = x^{*}\psi(a^{-}–b^{+}) - y^{*}\psi(a, b)$$

Excitation corresponds to the transition $\psi_{\mathrm{N}} \longrightarrow \psi_{\mathrm{E}}$. As the energy of excitation (measured by the wave-number of the maximum of the charge-transfer band) is large compared with the energy of the ground state, and as $x^{*} \gg y^{*}$ normally, the excitation energy within this series of complexes may be said, to a first approximation, to be proportional to the energy of the excited state, which is mainly the structure $\psi(a^{-}–b^{+})$. If in the ground state, either $x \ll y$, indicating that the ground state is essentially ionic, which is unlikely in the complexes being studied here, or, alternatively, the contribution of the no-bond function is present as a more or less constant fraction in the series of complexes, then the differences in the energy of the ground state (measured by the free energy of complex formation) may be attributed to the relative contribution of the dative structure $\psi(a^{-}–b^{+})$. This would account for the proportionality between the free energies of formation of the complexes and their excitation energies.

FIG. 3. *Absorption spectra of hexamethylbenene with* (*a*) *chloranil,* (*b*) *bromanil, and* (*c*) *iodanil in carbon tetrachloride solution, calculated from the spectra of equilibrium mixtures of the complexes with their components.*



The molar extinction coefficients of the complexes appear to be mainly of the order 2—2·5 × 10³. Where the steric effects of the complexes might be expected to be large, however, as in the case of iodanil and of duroquinone, the values of the extinction coefficients are considerably lower. The molar extinction coefficients for the hexamethylbenzene complexes of 2 : 6-dichloro- and 2 : 6-dimethyl-*p*-benzoquinone are higher than for the corresponding monosubstituted quinones, in which the steric effects would be expected to be less. It is interesting to note that both chloro-*p*-benzoquinone and toluquinone have low melting points. This suggests that these monosubstituted *p*-benzoquinones do not form very stable crystal lattices, which again may be due to the steric effects of their unsymmetrical molecules.

The charge-transfer spectra of most of the complexes measured show some fine structure similar to that of the hexamethylbenzene–2 : 6-dichloro-*p*-benzoquinone complex shown in Fig. 1. This has been found to be reproducible on different intruments and persists at low optical densities, which suggests that it is not an instrumental effect. In the case of the hexamethylbenzene–chloranil complex this observation of fine structure is in disagreement with the description given by Briegleb and Czekalla [3] of the same complex (also in carbon tetrachloride solution). They find only one maximum in the charge-transfer band, at 19,350 cm.$^{-1}$ which agrees well with the centre of the band-envelope obtained in our determination, namely, 19,300 cm.$^{-1}$. In the series of complexes of hexamethylbenzene with chloranil, bromanil, and iodanil, the band-width of the fine structure increases progressively (Fig. 3). The energies corresponding to these band-widths are proportional to the atomic excitation $^2P_{3/2} - {}^2P_{1/2}$ of the corresponding halogen atoms[20] (Table 4). However it seems unlikely that this correspondence could be given the same explanation as in the spectra of the alkali halides, for the separation of the peaks in the halide spectra is thought to be due to the formation of free halogen atoms during absorption, the two peaks corresponding to the production of halogen atoms in either the $^2P_{3/2}$ or the $^2P_{1/2}$ state.[20,21] The facts that the quinone complexes have spectra which show more than two peaks in the charge-transfer band and that hexamethylbenzene–2 : 6-dichloro-*p*-benzoquinone shows a band-width of fine structure of 28 mμ are difficult to interpret. Also the presence of fine structure in the charge-transfer band of the *p*-benzoquinone complex would require another explanation. It seems more likely that the fine structure results from electronic transitions corresponding to energy transitions in the quinones themselves, which have become modified by the proximity of the donor molecule in the complex. No fine structure has been observed in the case of the methyl-*p*-benzoquinone complexes.

TABLE 4. *Energies corresponding to the band-width of the fine structure in the charge-transfer bands of certain complexes.*

| | Atomic excitation[20] $^2P_{3/2} - {}^2P_{1/2}$ (ev) | Band-width of fine structure in tetrahalogeno-*p*-benzoquinone–hexamethylbenzene complexes (mμ) | Energy corresponding to band-widths in col. 3 (ev) |
|---|---|---|---|
| Chlorine ......... | 0·109 | 12 | 0·056 |
| Bromine ......... | 0·454 | 46 | 0·21 |
| Iodine ............ | 0·937 | 87 | 0·42 |

DYSON PERRINS LABORATORY, OXFORD UNIVERSITY.

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[20] Turner, *Phys. Rev.*, 1926, **27**, 397.
[21] Orgel, *Quart. Rev.*, 1954, **8**, 423.