Tetrahedron. 1960, Vol. 10, pp. 96 to 101. Pergamon Press Ltd. Printed in Northern Ireland

THE ABSORPTION SPECTRA OF MOLECULAR COMPLEXES

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(*Received* 30 *December* 1959)

Abstract—The intermolecular charge-transfer absorption spectra of complexes of various p-π aromatic electron donor molecules with a series of p-π aromatic electron acceptor molecules have been measured. The frequencies of the bands of these complexes may be expressed simply as the sum of two terms, characteristic of the donor and acceptor molecules respectively. This relationship fails if the electron donor is weak.

The molecular complexes between electron donors and electron acceptors usually show new electronic absorption transitions not observed in either component alone. One group of such interactions involves heats of formation in the ground state of the order 1–5 kcal/mole. These have been described by Mulliken[1] as outer complexes, and his interpretation that the new bands are intermolecular charge-transfer transitions is now generally accepted.

Many regularities in the absorption spectra have been observed: in particular McConnell *et al.*[2] have demonstrated the approximate linearity between the maximum extinction coefficient of the charge-transfer band (ε) and the wavelength at which this occurs (λ) for complexes of the donor benzene with various acceptors. The acceptors,

Table 1. Molar extinction coefficients (ε) and wavelengths (λ) of maximum absorption of hexamethylbenzene complexes in carbon tetrachloride

Acceptor	ε $(\text{l. mole}^{-1}\text{cm}^{-1})$	λ mμ	Ref.
Bromanil	2000	527	3
Chloranil	2500	518	3
Iodanil	1400	511	3
2,6-Dichloro-*p*-benzoquinone	2400	480	3
Chloro-*p*-benzoquinone	2000	442	3
1,2,3,5-Tetranitrobenzene	2300	425	4
p-Benzoquinone	2000	418	3
p-Toluoquinone	1800	409	3
1,2,4-Trinitrobenzene	1200	395	4
1,3,5-Trinitrobenzene	2500	395	4
Duroquinone	1200	393	3
2,6-Dimethyl-*p*-benzoquinone	2100	390	3
Iodine	8200	375	5
1,2,3-Trinitrobenzene	1500	350	4
Iodine monochloride	4000	334	5

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[1] R. S. Mulliken, *J. Chem. Phys.* **19**, 514 (1951); *J. Amer. Chem. Soc.* **72**, 600 (1950); **74**, 811 (1952).
[2] H. McConnell, J. S. Ham and J. R. Platt, *J. Chem. Phys.* **21**, 66 (1953).
[3] R. Foster, D. Ll. Hammick and P. J. Placito, *J. Chem. Soc.* 3881 (1956).
[4] R. Foster, *J. Chem. Soc.* In press.
[5] L. J. Andrews and R. M. Keefer, *J. Amer. Chem. Soc.* **74**, 4500 (1952).

though differing much between themselves, gave complexes whose λ values were all within 20 mμ. It is now possible to list a similar set of data, namely for the complexes of various acceptors with hexamethylbenzene in carbon tetrachloride solution, in which the range of λ is $\sim$190 mμ. There appears to be no correlation between λ and ϵ (Table 1). It is possible that any trend is masked by sterically bulky or asymmetrical groups in the acceptor molecule which would appear to lower ϵ while having little effect on λ. This behaviour is observed in donor molecules with a given acceptor; for example,[6] in dichloromethane, for the complex tetracyanoethylene-hexamethylbenzene, $\lambda = 545$ mμ, $\epsilon = 4390$; whereas for tetracyanoethylene-hexaethylbenzene, $\lambda = 550$ mμ, $\epsilon = 56$.

McConnell *et al.* were also able to show that the frequencies (ν) of charge-transfer band maxima for complexes of a series of donors with the acceptor iodine were proportional to the ionisation potentials (I) of the respective donors, thus:

$$\nu = a\mathrm{I} + b \tag{1}$$

and this was related to a theoretical expression:

$$\nu = \mathrm{I} - \mathrm{E} - \mathrm{W} \tag{2}$$

where E is the electron affinity of the acceptor molecule and W is the dissociation energy of the charge-transfer excited state. At the same time Hastings *et al.*[7] showed the relationship between ν for the complex and I for the donor molecule to be:

$$\mathrm{h}\nu = \mathrm{I} - c_1 + \frac{c_2}{\mathrm{I} - c_1} \tag{3}$$

where $c_1 = \mathrm{E} - e^2/r - \mathrm{C_{AB}}$, in which e^2/r is the coulomb attraction term and $\mathrm{C_{AB}}$ is the sum of all other energies; c_2 is a constant. Briegleb and Czekalla[8] have used such relationships to correlate ν for complexes of various donors with the electron acceptors: iodine, 1,3,5-trinitrobenzene and chloranil. There is good agreement between the values of ν and I's for the donor molecules. The absorption bands of complexes of chloranil with donors of accurately known ionization potential have now been remeasured in carbon tetrachloride solution and the values of ν plotted against Watanabe's[9] values of I for the donors (Fig. 1).

A reliable value for the naphthalene complex could not be obtained because of the coincidence of a fluorescence emission band of naphthalene with the charge-transfer absorption band of the complex. The least squares line gives a rather better fit than does the particular quadratic function proposed by Briegleb and Czekalla. It may be argued that some deviation should be expected because of the only approximate equality of the energy of the transition with the frequency of maximum absorption of a broad band. A maximum difference between the two correlations for chloranil complexes will be shown for complexes which have an absorption band at or about 700 mμ. For example perylene-chloranil in carbon tetrachloride has $\nu = 14200$ cm^{-1} (1·75 eV). The quadratic curve indicates 7·15 eV whilst the linear curve predicts 6·95 eV as the ionization potential of perylene, for which Hedges and Matsen[10] have calculated a value of 6·94 eV.

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[6] R. E. Merrifield and W. D. Phillips, *J. Amer. Chem. Soc.* **80**, 2778 (1958).

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

[8] G. Briegleb and J. Czekalla, *Z. Electrochem.* **63**, 6 (1959).

[9] K. Watanabe, *J. Phys. Chem.* **22**, 1564 (1954); **26**, 184 (1957).

[10] R. M. Hedges and F. A. Matsen, *J. Chem. Phys.* **28**, 950 (1958).

Complexes formed from electron donors of low ionisation potential and acceptors of high electron affinity usually have favourable equilibrium constants and have the charge-transfer absorption bands at relatively long wavelengths often well separated from the absorption bands of the components themselves; this enables ν to be easily determined experimentally. Unfortunately neither electron affinities of aromatic acceptor molecules, nor ionisation potentials of many aromatic donor molecules of low ionisation potential have been measured. For this reason comparisons have been made of ν where either the donor or the acceptor is varied in a series of complexes.

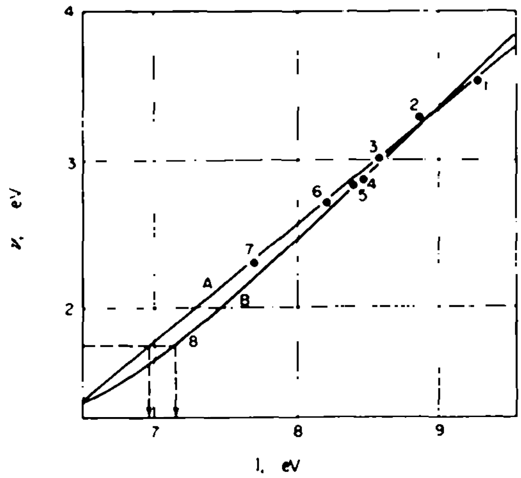

FIG. 1. Frequencies (ν) of charge-transfer bands of chloranil complexes of the donors: (1) benzene, (2) toluene, (3) *o*- and *m*-xylene, (4) *p*-xylene, (5) mesitylene, (6) anisole, (7) aniline, against the ionisation potentials (I) of these donors as correlated by (A) the least squares line (B) Briegleb and Czekalla's quadratic function. Two possible interpolated values of I for perylene are shown (8) (solvent carbon tetrachloride).

Consider the plots of $\nu_{1,y}$ of complexes of a given donor (1) with a series of acceptors (y) against $\nu_{2,y}$ of complexes of these acceptors with a second donor (2). It is implicit in equation (1) that these ν's will be related by a straight line of unit gradient provided that the parameter a in equation (1) is independent of the acceptor molecule. This condition appears to hold for the relatively strong complexes presently studied, viz.:

$$\nu_{2,y} = \nu_{1,y} + f \tag{4}$$

These are the complexes formed from the aromatic donors: hexamethylbenzene, N-methylaniline, N, N-dimethylaniline, N,N,N',N', tetramethyl-*p*-diaminodiphenylmethane (tetrabase), N,N,N',N', tetramethyl-*p*-phenylenediamine (Wurster's base), with the aromatic acceptors *m*-dinitrobenzene, 2,4,6-trinitrotoluene 1,3,5-trinitrobenzene, *p*-benzoquinone, chloro-*p*-benzoquinone, 2,6-dichloro-*p*-benzoquinone, chloranil. Certain other acceptors such as iodine and tetracyanoethylene were not included because of their irreversible action on the amines (but see below). All the spectra were measured in cyclohexane solution. Evans[11] has suggested that this may act as a donor, perhaps by promoting contact charge-transfer absorption[12] This does not appear to affect ν for the interactions studied which values correspond closely to

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[11] D. F. Evans, *J. Chem. Phys.* 23, 1424 (1955).

[12] L. E. Orgel and R. S. Mulliken, *J. Amer. Chem. Soc.* 79, 4839 (1957).

those obtained in carbon tetrachloride solution. Use of the former solvent is advantageous in its greater transparency and in that complex formation is more favoured than in carbon tetrachloride.

The plots of equation (4) are given in Fig. 2. Equation (4), being linear, implies that *a* in equation (1) is independent of the particular acceptor: from Fig. 1, *a* may be taken as 0·85. Also, because of the linearity of equation (4), for a given donor, ν must be proportional to some function of the acceptor molecule which we may define as *e* in equation (5) and call the apparent electron affinity. This term *e* will include some measure of the bond dissociation energy W of equation (2).

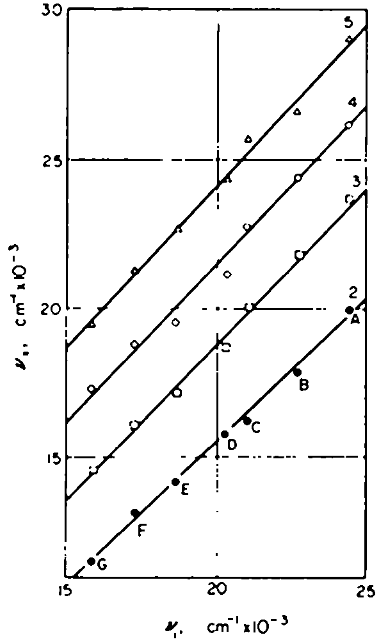

FIG. 2. Frequencies of the charge-transfer band (ν_x) of complexes of the donors: (2) Wurster's base, (3) tetrabase, (4) N-methylaniline, (5) hexamethylbenzene, with the series of acceptors: (A) *m*-dinitrobenzene, (B) 2,4,6-trinitrotoluene, (C) 1,3,5-trinitrobenzene, (D) *p*-benzoquinone (E) chloro-*p*-benzoquinone, (F) 2,6-dichloro-p-benzoquinone, (G) chloranil, against the frequencies of the charge-transfer bands (ν_1) of the complexes of these acceptors with N,N-dimethylaniline (solvent cyclohexane).

All the present results may therefore be related by the equation:

$$\nu = 0{\cdot}85\,\mathrm{I} - e \tag{5}$$

Selection of appropriate values of I and *e* to fit ν values of the complexes of the series of acceptors with one donor and the series of donors with one acceptor then enable the remaining ν's to be interpolated by equation (5) (Table 2).

The regularities, due to *a* in equation (1) being independent of the acceptor, cannot include the tetracyanoethylene complexes[6] (in dichloromethane) where $a = 0{\cdot}487$. The results for iodine complexes are conflicting: for polynuclear aromatics[13] $a = 0{\cdot}86$ (based on calculated I values), whereas for the iodine complexes related by McConnell *et al.*[2], $a = 0{\cdot}64$. Large deviations from straight lines of unit gradient in the plots of

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[13] P. Bhattacharya and S. Basu, *Trans. Faraday Soc.* **54**, 1286 (1958).

TABLE 2. FREQUENCIES OF CHARGE-TRANSFER MAXIMA (ν)* OF COMPLEXES IN CYCLOHEXANE INTERPOLATED FROM THE IONIZATION POTENTIALS (I) OF THE DONORS AND THE APPARENT ELECTRON AFFINITIES (e) OF THE ACCEPTORS

(obtained from the complexes of donors with chloranil, and acceptors with N,N-dimethylaniline from equation (5), I(N,N-dimethylaniline) assumed to be 7·20 eV)
Measured values of ν in parentheses

Acceptor	Donor	Wurster's base	Tetrabase	N-Methylaniline	Hexamethylbenzene
	I(eV)	6·67	7·05	7·38	7·67
	e(eV)				
2,6-Dichloro-*p*-benzoquinone	4·36	1·59 (1·63)	1·97 (1·99)	2·30 (2·32)	2·59 (2·63)
Chloro-*p*-benzoquinone	4·19	1·76 (1·75)	2·14 (2·12)	2·47 (2·41)	2·76 (2·80)
Quinone	3·98	1·97 (1·95)	2·35 (2·31)	2·68 (2·62)	2·97 (3·01)
1,3,5-Trinitrobenzene	3·89	2·06 (2·01)	2·44 (2·48)	2·77 (2·81)	3·06 (3·18)
2,4,6-Trinitrotoluene	3·68	2·27 (2·21)	2·65 (2·69)	2·98 (3·01)	3·27 (3·28)
m-Dinitrobenzene	3·47	2·48 (2·47)	2·86 (2·92)	3·19 (3·23)	3·48 (3·59)

* Values are in eV.

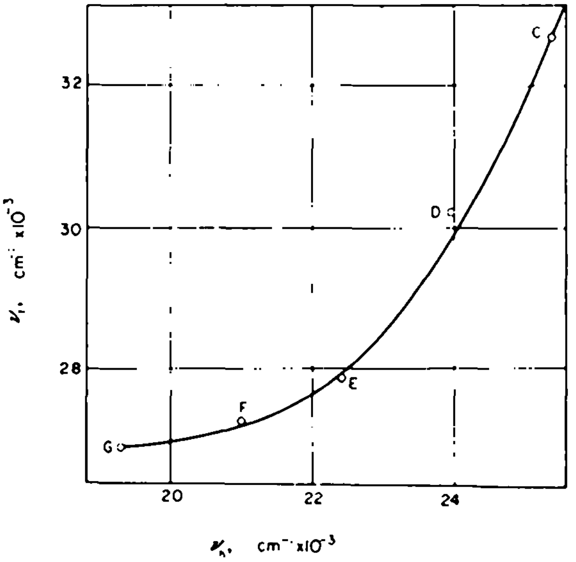

FIG. 3. Frequencies of charge-transfer bands (ν_t) of toluene complexes of a series of acceptors against the frequencies of the charge-transfer bands (ν_h) of the complexes of hexamethylbenzene with the same series of acceptors (identified by the same letters as in Fig. 2) (solvent carbon tetrachloride).

equation (5) appear if the electron donor is only weakly effective. This is seen in the plot of ν for the complexes of the weak donor toluene ($I = 8{\cdot}82$ eV) when plotted against ν for hexamethylbenzene complexes (Fig. 3).

EXPERIMENTAL

All melting points measured on a Kofler hot-stage.

Materials and solvents. Carbon tetrachloride and cyclohexane were B.D.H. spectroscopic grade, used without further purification.

Hexamethylbenzene. Prepared by Cullinane and Chard's method,[14] recrystallized five times from ethanol, m.p. 164°.

N,N-*Dimethylaniline.* B.D.H. AnalaR grade refluxed with acetic anhydride, washed five times with water, dried and distilled.

N-*Methylaniline.* B.D.H. AnalaR grade purified by the N-nitroso compound.

Tetrabase. Recrystallized four times from methanol, m.p. 91°.

Wurster's base. Prepared from the recrystallized dihydrochloride and distilled *in vacuo*, m.p. 51°.

m-*Dinitrobenzene.* B.D.H. analytical grade, recrystallized twice from carbon tetrachloride, m.p. 91°.

2,4,6-*Trinitrotoluene.* Recrystallized four times from carbon tetrachloride, m.p. 80·5°.

1,3,5-*Trinitrobenzene.* Recrystallized once from aqueous ethanol and thrice from carbon tetrachloride, m.p. 123°.

Chloro-p-*benzoquinone.* Prepared by Conant and Fieser's method,[15] recrystallized thrice from ethanol, m.p. 57°.

2,6-*Dichloro*-p-*benzoquinone.* Prepared by Faust's method,[16] recrystallized thrice from ethanol m.p. 120°.

Chloranil. Recrystallized four times from benzene, m.p. 289°.

Analytical. All spectra save those with absorption maxima at wavelengths longer than 720 mμ were measured on an Optica CF4 grating spectrophotometer. Above this wavelength a Unicam SP 500 was used. For each determination two basic solutions were made up: a solution 0·05–0·3 M of the donor, and a solution 10^{-3}–10^{-4} M of the acceptor. Equal volumes of these two solutions were mixed and two 1 cm fused silica cuvettes filled and placed *in tandem* in the cell compartment. In the compensating beam two cells were similarly placed, one containing the basic donor solution, the other the basic acceptor solution. The absorption measured is the difference between the unmixed and the mixed components; it is assumed that in the complex the charge-transfer band occurs in addition to the transition characteristic of the components. In most cases, because of the complexes selected, the charge-transfer band was at considerably longer wavelengths than the absorption of the components, but this technique enabled the band to be resolved in unfavourable cases. Determinations were repeated using different concentrations of donor and acceptor. All measurements were made at room temperature (18–20°).

In no case was any fine structure observed even with slit widths of 0·01 mm. This includes the spectra of the quinone-hexamethylbenzene complexes which we had previously claimed to possess fine structure.[3]

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[14] N. M. Cullinane and S. J. Chard, *J. Chem. Soc.* **821** (1945).

[15] J. B. Conant and L. F. Fieser, *J. Amer. Chem. Soc.* **45**, 2204 (1923).

[16] A. Faust, *Liebigs Ann.* **149**, 153 (1869).