The Absorption Spectra of the Molecular Complexes of Aromatic Compounds with p-Bromanil

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The characteristic absorption spectra of molecular complexes have already been interpreted by the charge transfer theory of Mulliken[1,2]. By the approximation of the theory, the parabolic or linear relation between the energy of the charge transfer transition ($h\nu$) and the ionization potential of the donor (I_p) has been derived and experimentally confirmed[3-6].

$$h\nu = I_p - c_1 + \frac{c_2}{I_p - c_1} \tag{1}$$

$$h\nu = aI_p + b \tag{2}$$

Here, a, b, c_1 and c_2 are assumed to be characteristic constants for the complexes of any one acceptor. Equation 1 is based on Mulliken's theory more strictly than is Eq. 2. However, for weak complexes where the third term in Eq. 1 is rather small, the simple form of Eq. 2 can be a sufficient approximation.

If the coefficients in these equations are known for complexes of various acceptors, the positions of the charge transfer bands in the absorption spectra of the complexes can be predicted from the ionization potentials of donors, or vice versa; also, a comparison of the so-called "apparent electron affinities"[6] of the acceptors can be made. Therefore, it is desirable to obtain these relations in many series of complexes. In this short note, the coefficients of Eq. 2 are determined for the complexes of aromatic hydrocarbons and amines with *p*-bromanil, and the ionization potentials of several donors are estimated.

The charge transfer spectra of the complexes were measured in a carbon tetrachloride solution by the use of a Cary model-11 spectrophotometer at room temperature. The observed results are summarized in Tables I and II, along with the ionization potentials of the donors, which have been given by Watanabe[7] and by Briegleb and Czekalla[4]. Using these ionization potentials, we obtained the following relations:

$$h\nu = 0.928 I_p - 4.95 \text{ eV.} \tag{3}$$

for the complexes of the polycyclic aromatic hydrocarbons in Table I, and

$$h\nu = 0.973 I_p - 5.27 \text{ eV.} \tag{4}$$

for the complexes of the substituted aromatic compounds. On the other hand, Foster[6] has examined the absorption spectra for many molecular complexes with several acceptors and has shown that coefficient "a" in Eq. 2

TABLE I. MAXIMA OF CHARGE TRANSFER BANDS FOR COMPLEXES OF POLYCYCLIC AROMATIC HYDROCARBONS WITH *p*-BROMANIL IN CARBON TETRACHLORIDE

No.	Donor	Maximum of charge transfer band		Ionization potential[a], eV.
		λ, mμ	$h\nu$, eV.	
1	Naphthalene	486	2.55	8.12[b]
2	Anthracene	630	1.97	7.4
3	Phenanthrene	465	2.67	8.1
4	Pyrene	608	2.04	7.55
5	Chrysene	562	2.21	7.8
6	Triphenylene	487	2.55	8.1
7	1,2-Benzanthracene	587	2.11	7.6
8	Perylene	738	1.68	7.15
9	Anthanthrene	756	1.64	—

a) from Ref. 4 b) from Ref. 7

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TABLE II. MAXIMA OF CHARGE TRANSFER BANDS FOR COMPLEXES OF SUBSTITUTED AROMATIC COMPOUNDS WITH *p*-BROMANIL IN CARBON TETRACHLORIDE

No.	Donor	Maximum of charge transfer band		Ionization potential[a)], eV.
		λ, mμ	$h\nu$, eV.	
10	1-Methylnaphthalene	418 503	2.97 2.46_5	7.96[b)]
11	Acenaphthene	566	2.19	—
12	Diphenyl	410	3.02	8.45
13	*p*-Xylene	424	2.92	8.445[b)]
14	Mesitylene	421	2.94_5	8.39[b)]
15	Aniline	560	2.21	7.70[b)]
16	Dimethylaniline	657	1.89	7.3
17	*p*-Chloroaniline	500	2.48	—
18	*o*-Phenylenediamine	638	1.94	7.45
19	Diphenylamine	655	1.89	7.4
20	Phenyl-α-naphthylamine	718	1.73	—
21	Phenyl-β-naphthylamine	706	1.75_6	—
22	α-Naphthylamine	632	1.96	7.4
23	*p*-Toluidine	586	2.12	7.65
24	*o*-Toluidine	558	2.22	7.75
25	Phenothiazine	665 > 800	1.86_5 —	—
26	Acridine	493	2.51_6	—

a) from Ref. 4 b) from Ref. 7

is usually 0.85. If we use this value as "*a*", coefficient "*b*", or the apparent electron affinity for the present acceptor, can be calculated as −4.32 eV. by the method of the least squares.

$$h\nu = 0.85 I_p - 4.32\ \text{eV}. \qquad (5)$$

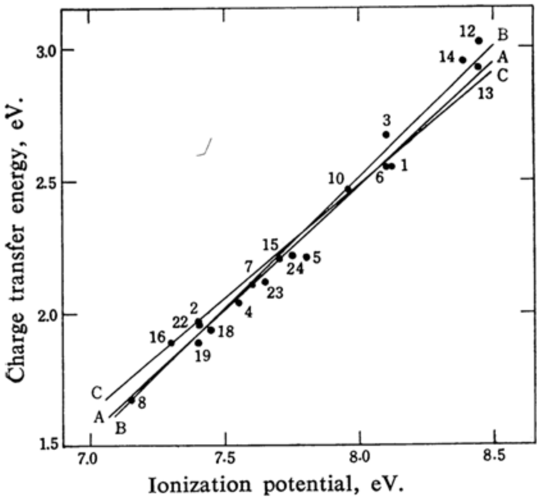

Fig. 1. Plot of energy of charge transfer absorption versus ionization potential. Donors are represented by the corresponding number in Tables I and II.

A : $h\nu = 0.927 I_p - 4.95$
B : $h\nu = 0.973 I_p - 5.27$
C : $h\nu = 0.85 I_p - 4.32$

TABLE III. IONIZATION POTENTIALS OF DONORS ESTIMATED FROM EQ. 5

Donor	Ionization potential calculated from Eq. 5, eV.
Naphthalene	8.08
Anthracene	7.40
Phenanthrene	8.22
Pyrene	7.48
Chrysene	7.68
Triphenylene	8.08
1,2-Benzanthracene	7.56
Perylene	7.06
Anthanthrene	7.01
1-Methylnaphthalene	7.98
Acenaphthene	7.66
Diphenyl	8.64
p-Xylene	8.52
Mesitylene	8.55
Aniline	7.68
Dimethylaniline	7.31
p-Chloroaniline	8.00
o-Phenylenediamine	7.36
Diphenylamine	7.31
Phenyl-α-naphthylamine	7.12
Phenyl-β-naphthylamine	7.15
α-Naphthylamine	7.39
p-Toluidine	7.58
o-Toluidine	7.69
Phenothiazine	7.28
Acridine	8.04

As is shown in Fig. 1, no serious difference is found between these equations in the I_p range from 7.0 to 8.5 eV. In consequence, a comparison of the apparent electron affinity of the acceptor can be conveniently made by using the last equation. The apparent electron affinity of *p*-bromanil is slightly larger than that of *p*-chloranil, 4.16 eV.; this seems to be quite reasonable. The ionization potentials of the donors, which were determined from the observed charge transfer energy in association with Eq. 5, are given in Table III.

Among the complexes of polycyclic aromatic hydrocarbons, perylene and pyrene gave crystalline complexes with *p*-bromanil. Their charge transfer bands were found at 755 and 650 mμ respectively, by employing the KBr-disk method. The solid complexes of some aromatic amines, such as tetramethyl-*p*-phenylenediamine, dimethylaniline, etc., with *p*-bromanil have been found to give electron spin resonance absorptions[8-10]. However, the complexes of perylene and pyrene with *p*-bromanil were found to give no electron spin resonance in their crystalline state. Considering that perylene and pyrene possess nearly the same ionization potential values as the amines, the difference in the magnetic property of the molecular complexes can not be explained simply by the difference in the ionization potential of the donors.

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