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NEW DESCRIPTION OF THE SUBSTITUENT EFFECT ON ELECTRONIC SPECTRA BY MEANS OF SUBSTITUENT CONSTANTS. III. CHARGE TRANSFER SPECTRA OF EDA COMPLEXES

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Abstract General equations in order to describe the electronic spectra by means of substituent constants were derived on the basis of molecular orbital theory. The most suitable substituent constants are theoretically Swain's F and R constants, but Yukawa-Tsuno's parameter is also useful for π-electron system. In this paper these equations were applied to explain the charge transfer spectra of π-π type EDA complexes composed of TCNE and various kinds of aromatic donors. The results have been quite reasonable and discussed in detail.

INTRODUCTION

In earlier papers we derived the Eq. 1 given below that connects the nonaqueous oxidation $(E^{oxd}_{1/2})$ and reduction $(E^{red}_{1/2})$ potentials and electronic singlet or triplet band energy, the latter being mainly contributed from HOMO→LUMO transition and having the same character in a series of substances.[1-4]

$$(E^{oxd}_{1/2} - E^{red}_{1/2}) = k_1 \cdot {}^{1,3}E^{UV}_{ho\rightarrow lu} + k_2 \qquad (1)$$

The physical meaning of the constant terms, k_1 and k_2, was quantitatively interpreted,[1] and many experimental results have well fulfilled the theoretical prediction due to the Eq. 1.[1-6] Now, it is well known that the $E^{oxd}_{1/2}$ and $E^{red}_{1/2}$, corresponding to the free energy change of redox reactions, are explained by the so-called substituent constants[7] but in different way between $E_{1/2}^{oxd}$ and $E_{1/2}^{red}$.[1-6] These facts should be ascribed to that the electronic transition band is written by the energy difference between ground and excited states, each of which behaves in different way for the substituent effect. Those circumstances render the description of UV band energy by the usual substituent constants like σ_p, σ_m etc. difficult. However, it should be noted that Swain and his colleaques derived theoretically and experimentally their F and R substituent constants,[8-9] use of which makes it possible to write the various kinds of substituent constants (σ_p, σ_m, σ^+, σ^-, σ^* and so on) for aromatic and aliphatic systems by the form of equation $\sigma = fF + rR + c$. Applying this equation to Eq. 1, we derived Eq. 2, the limitation and the scope of Eq. 2 was already discussed in detail.[6,10]

$$^{1,3}E^{UV} = aF + bR + c \qquad (2)$$

In turn, the same process as the derivation of Eq. 2 indicates that the Eq. 3 instead of Eq. 2 is also useful for π-electron system alone, where σ_i, σ_π^+ and σ_π^- are Yukawa-Tsuno's substituent constants.[11-12] It was verified that the substituent constants such as σ^+, σ^-, σ_p, σ_m and σ_p° are also written by the linear combination of σ_i, σ_π^+ and σ_π^-.[11-12]

$$^{1,3}E^{UV} = \alpha\sigma_i + \beta\sigma_\pi^+ + \gamma\sigma_\pi^- + c \qquad (3)$$

In order to certify and to develop Eqs. 2 and 3 the application of these equations to the intermolecular charge transfer bands (CT bands) has been studied in this paper. At first we have carefully recorded the CT bands due to the π-π type EDA complexes in CH_2Cl_2 composed of tetracyanoethylene (TCNE) as an electron acceptor and various kinds of substituted benzenes and stilbenes as electron donors. According to

Mulliken's charge transfer theory[13] the CT band energy inherent to the CT complexes pertinent to the above systems is written by Eq. 4 based on perturbation theory.

$$h\nu_{CT} = (I_P - c_1) + [c_2/(I_P - c_1)] \quad (4)$$

Since the second term value in the right-hand side of Eq. 4 is much smaller than the first term value in the case of weak complexes, Eq. 4 is then rewitten as Eq. 5, where c_3 is a new constant, and I_P is the vertical ionization potential of electron donors.

$$h\nu_{CT} = I_P - c_3 \quad (5)$$

The I_P and nonaqueous $E_{1/2}^{oxd}$ values are the physical constants quite similar to each other, because the relation of Eq. 6 is well kown.[1]

$$E_{1/2}^{oxd}\ (R^{\dot{+}}/R) = -\varepsilon_{ho} + \Delta G^\circ + \Delta E_{solv}^{\dot{+}} \quad (6)$$

Where ΔG°, $\Delta E_{solv}^{\dot{+}}$, and ε_{ho} ($I_P = -\varepsilon_{ho}$) are the absolute potential of reference electrode, solvation energy difference between cation radical and neutral species, and HOMO energy, respectively. The values of $\Delta E_{solv}^{\dot{+}}$ are not so varied in a series of similar substances, therefore we can easily predict that the I_P values having the same character in a series of substances, in other words, $h\nu_{CT}$ values according to Eq. 5 are also expressed by Eq. 2 or 3 by means of substituent constants.

RESULTS AND DISCUSSION

Substituted benzenes (see TABLE I), TCNE, and CH_2Cl_2(solvent of spectrograde purity) commercially available were carefully purified by a usual manner. Pure stilbene derivatives (see TABLE II) used here are the same as those employed in our

TABLE I The $h\nu_{CT}$ values of substituted benzenes - TCNE complexes,[a] and I_P values[b] of the benzene derivatives.

No.	Substituent	$h\nu_{CT}(1)$		$h\nu_{CT}(2)$		I_P
		(nm)	(eV)	(nm)	(eV)	(eV)
1.	H(benzene)	386.4	3.209			9.23
2.	mono-CH_3	409.8	3.026			8.85
3.	mono-C_2H_5	411.0	3.017			
4.	mono-Cl	367.7	3.372			
5.	mono-Br	384.0	3.229			
6.	mono-OH	495.8	2.501	393.4	3.152	8.73
7.	mono-OCH_3	506.8	2.446	387.2	3.202	8.39
8.	mono-OC_2H_5	515.3	2.406	389.2	3.186	
9.	mono-NH_2	583.8	2.124			8.05
10.	mono-$N(CH_3)_2$	674.5	1.838	402.8	3.078	7.37
11.	mono-COOH	340.0	3.647			
12.	mono-$COOCH_3$	339.7	3.650			
13.	mono-$COOC_2H_5$	337.2	3.677			
14.	mono-CF_3	327.6	3.785			
15.	p-$CH_3 \cdot Cl$	430.0	2.883			
16.	p-$CH_3 \cdot Br$	441.2	2.810			
17.	p-$CH_3 \cdot OH$	534.9	2.318	393.1	3.154	
18.	p-$Cl \cdot Cl$	400.8	3.093			
19.	p-$Cl \cdot OH$	505.3	2.454			
20.	p-$Cl \cdot NH_2$	589.2	2.104			
21.	p-$Br \cdot Br$	412.2	3.008			
22.	p-$Br \cdot OH$	500.5	2.477	355.8	3.485	
23.	p-$Br \cdot OCH_3$	513.7	2.414	355.9	3.484	
24.	p-$Br \cdot NH_2$	597.1	2.076			
25.	p-$OH \cdot OCH_3$	621.8	1.994	379.9	3.264	
26.	p-$OCH_3 \cdot OCH_3$	631.6	1.963	378.8	3.273	
27.	p-$OCH_3 \cdot COOC_2H_5$	444.2	2.791	375.2	3.305	

a) Our spectral measurements were carried out by focusing the special attention on the first band of CT spectra. The second CT bands listed in this table are only those, which are clearly recorded in the course of the first CT band measurement.

b) See ref. 14 in the text. These are first I_P having the benzene e_{1g}(s) character.

TABLE II The $h\nu_{CT}$ values of 4,4'-disubstituted stilbenes - TCNE complexes,[a] and $E_{1/2}^{oxd}$ values[b] of the stilbene derivatives.

No.	Substituent	$h\nu_{CT}(1)$		$h\nu_{CT}(2)$		$E_{1/2}^{oxd}$
		(nm)	(eV)	(nm)	(eV)	(V *vs*. SCE)
1.	H(stilbene)	592.2	2.094	378.0	3.280	1.476
2.	4,4'-$(CH_3)_2$	660.0	1.879			1.225
3.	4,4'-$(C_2H_5)_2$	665.0	1.864	392.0	3.163	1.321
4.	4,4'-Cl_2	576.1	2.152			1.547
5.	4,4'-Br_2	577.0	2.149			1.605
6.	4,4'-$(OCH_3)_2$	776.1	1.598	~427.0	~2.904	0.996
7.	4,4'-$(OCOCH_3)_2$	585.0	2.119			1.453

a) See footnote a) in the TABLE I.

b) Taken from ref. 6 in the text. Solvent is CH_3CN.

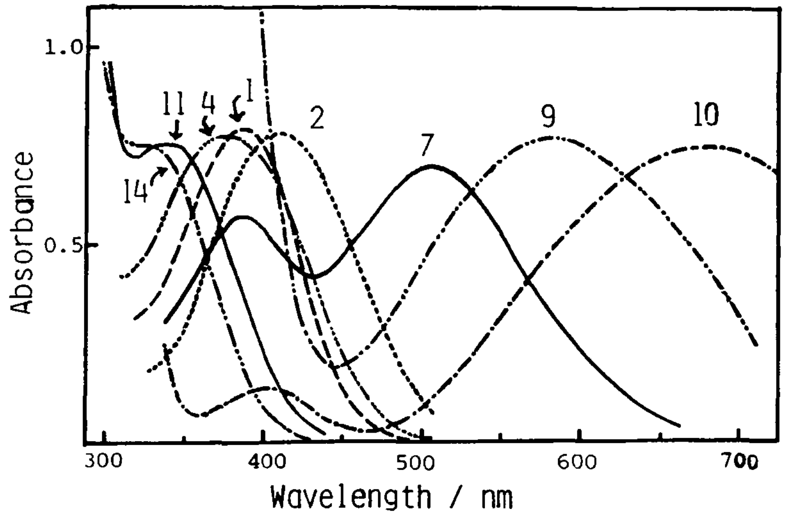

FIGURE 1. Charge transfer spectra pertinent to the monosubstituted benzenes - TCNE complexes in CH_2Cl_2. The number given in this figure denotes the sample number listed in TABLE I.

previous studies.[6] All the CT spectra were recorded at room temperature except for the systems consisting of TCNE and aniline or dimethylaniline, the latter systems being measured under the low temperature of dry ice-acetone because of the unstability of the complexes. All the experimental data, ionization potentials, and $E_{1/2}^{oxd}$ values are collected in TABLEs I and II, and the typical CT spectra are illustrated in Fig. 1.

Substituent Dependence of Ionization Potentials

At first the substituent dependence of ionization potentials has been examined on the several systems. In case of the I_P (eV unit) derived from benzene e_{1g}(s) level[14] the regression equation with F and R constants is $I_P = 0.434F + 0.502R + 9.126$ (sample number (n) = 9, correlation coefficient (r) = 0.9748, standard deviation (s) = 0.2334; $N(CH_3)_2$, NH_2, OCH_3, OH, CH_3, H, $COCH_3$, CN, NO_2). Also, for 4-substituted pyridine *N*-oxides the first I_P due to π-MO (b_1 under C_{2v}) contributed mainly from the *N*-oxide group oxygen 2pπ-AO[15] is $I_P = 0.354F + 0.372R + 8.305$ (n = 7, r = 0.9927, s = 0.095), and the nitrogen lone pair I_P of alkyl substituents of $N(R_1R_2R_3)$[16] is $I_P = 1.938F + 1.816R + 10.532$ (n = 7, r = 0.9676, s = 0.2853) by assuming the additivity of F and R constants. The description of I_P by means of F and R parameters seems to be very good.

Substituent Dependence of Charge Transfer Spectra

Let us now discuss the substituent effect on the CT spectra studied here by using Eqs. 2, 3 and 5. An example of Eq. 2 is shown in Fig. 2 for monosubstituted benzenes, where we can see that the agreement between observed and estimated CT spectral values is very good. The regression equation is

$$h\nu_{CT} = 0.269F + 0.454R + 3.204. \quad (7)$$
$$(n = 13,\ r = 0.9885,\ s = 0.1039)$$

The regression analyses similar to the above were also made on the other data listed in TABLE I. The results are as follows.

$$h\nu_{CT} = 0.0124F + 0.355R + 3.134 \quad (8)$$
$$(n = 14,\ r = 0.9832,\ s = 0.0843)$$

for *p*-disubstituted benzenes - TCNE complexes, and

$$h\nu_{CT} = 0.0290F + 0.415R + 3.249 \quad (9)$$
$$(n = 26,\ r = 0.9784,\ s = 0.1212)$$

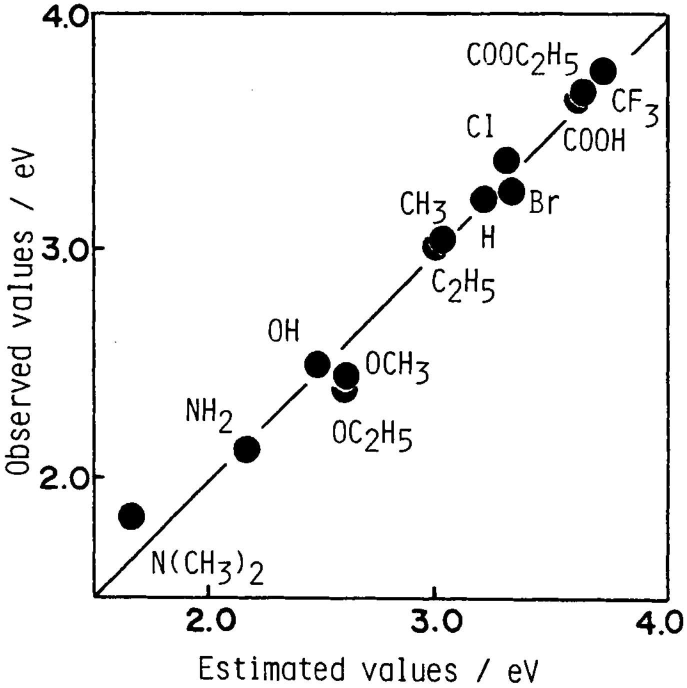

FIGURE 2. The correlation of observed and estimated CT band energies of monosubstituted benzene - TCNE complexes. The latter values are calculated from Eq. 7. See the text for details.

for all of the TCNE complexes of monosubstituted and *p*-disubstituted benzenes, the additivity of F and R values being assumed for the *p*-disubstituents. The relation of Eq. 9 is depicted in Fig. 3. In case of 4,4'-disubstituted stilbenes listed in TABLE II the regression equation is

$$h\nu_{CT} = 0.212F + 0.338R + 2.043. \qquad (10)$$

$$(n = 7,\ r = 0.9826,\ s = 0.0469)$$

Also, the application of Eqs. 3 and 5 to the system of monosubstituted benzenes gave the Eqs. 11 and 12, respectively,

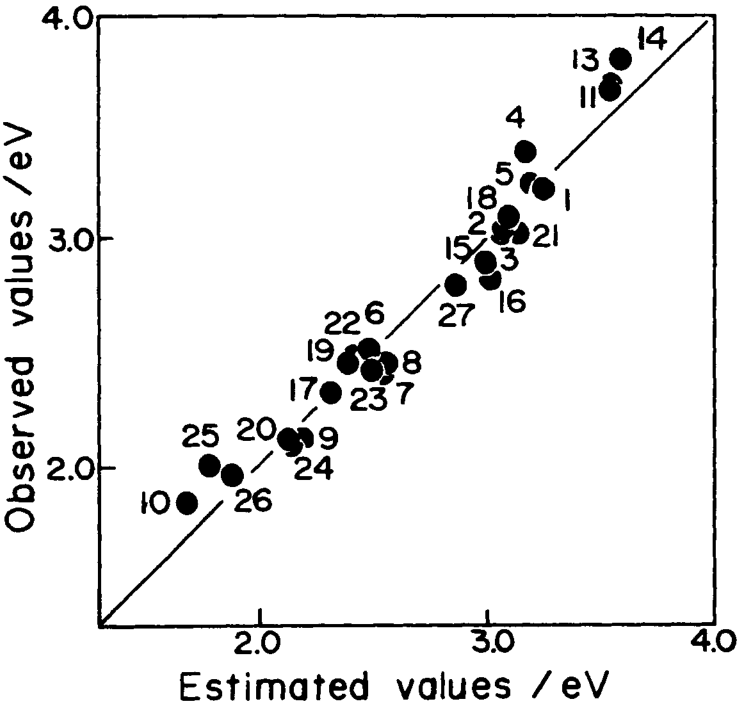

FIGURE 3. The correlation of observed and estimated CT band energies of substituted benzenes - TCNE complexes. The estimated values are obtained from Eq. 9. The number given in this figure denotes the sample number listed in TABLE I.

with quite good results.

$$h\nu_{CT} = 0.722\sigma_i + 2.729\sigma_\pi^+ + 1.456\sigma_\pi^- + 3.229 \quad (11)$$
$$(n = 10,\ r = 0.9921,\ s = 0.0985)$$

$$h\nu_{CT} = 0.792\ I_P - 4.108 \quad (12)$$
$$(n = 5,\ r = 0.9790,\ s = 0.1371)$$

The I_P data available here for explaining the $h\nu_{CT}$ was only 5 for monosubstituted benzenes.[14] When we have applied $E^{oxd}_{1/2}$ instead of I_P to correlate $h\nu_{CT}$, the Eq. 13 is obtained for 4,4'-disubstituted stilbenes. The linearity between $h\nu_{CT}$ and $E^{oxd}_{1/2}$ values is very good.

$$h\nu_{CT} = 0.960E^{oxd}_{1/2} + 0.660 \quad (13)$$
$$(n = 7,\ r = 0.9738,\ s = 0.0520)$$

Now, from the above results montioned hitherto it is easily understood that the $h\nu_{CT}$ values pertinent to the π-π type TCNE complexes are well described by means of Eqs. 2, 3 and 5, so that the $h\nu_{CT}$ values can be estimated with a good accuracy by using the substituent constants suggested here without the knowledge of ionization potentials. We are now extending this kind of study to the spectral and thermodynamical data of EDA complexes, like n-σ type, other than π-π type complexes.

REFERENCES

1. T. Kubota, H. Miyazaki, M. Yamakawa, K. Ezumi, and Y. Yamamoto, Bull. Chem. Soc. Jpn., 52, 1588 (1979).
2. T. Kubota, H. Miyazaki, K. Ezumi, and M. Yamakawa, Bull. Chem. Soc. Jpn., 47, 491 (1974).
3. T. Kubota and H. Miyazaki, Bunsekikiki, 11, 639 (1973).
4. T. Kubota, H. Miyazaki, and M. Yamakawa, Bull. Chem. Soc. Jpn., 45, 780 (1972).
5. T. Matsumura-Inoue, H. Tomono, M. Kasai, and T.Tominaga-Morimoto, J. Electroanal. Chem., 95, 109 (1979).
6. T. Kubota, B. Uno, Y. Matsuhisa, H. Miyazaki, and K.

Kano, Chem. Pharm. Bull., 31, 373, (1983).

7. P. Zuman, Substituent Effects in Organic Polarography (Plenum Press, New York, 1967).
8. C. G. Swain, S. H. Unger, N. R. Rosenquist, and M. S. Swain, J. Am. Chem. Soc., 105, 492 (1983).
9. C. G. Swain and E. C. Lupton, J. Am. Chem. Soc., 90, 4328 (1968).
10. B. Uno, Y. Matsuhisa, K. Kano, and T. Kubota, Chem. Pharm. Bull., 32, 1961 (1984).
11. M. Sawada, M. Ichimura, Y. Yukawa, T. Nakachi, and Y. Tsuno, Bull. Chem. Soc. Jpn., 53, 2055 (1980).
12. Y. Tsuno, M. Sawada, T. Fujii, and Y. Yukawa, Bull. Chem. Soc. Jpn., 52, 3033 (1979).
13. R. S. Mulliken and W. B. Person, Molecular Complexes — A Lecture and Reprint Volume (Wiley-Interscience, New York, 1969).
14. T. Kobayashi and S. Nagakura, Bull. Chem. Soc. Jpn., 47, 2563 (1974).
15. J. P. Maier and J-F. Muller, J. Chem. Soc. Faraday II, 70, 1991 (1974).
16. D. H. Aue, H. M. Webb, and M. T. Bowers, J. Am. Chem. Soc., 98, 311 (1976).